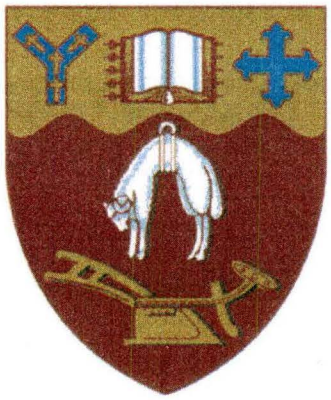
POLYNUCLEAR COMPLEXES WITH MACROCYCLIC LIGANDS



A thesis submitted
in partial fulfilment of the requirements
for the degree of
Doctor of Philosophy in Chemistry
by

Jan Wikaira

University of Canterbury

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"The great discoveries in Science are not accompanied by 'Eureka I've found it' but rather by 'Hmmm, that's funny'"

- Isaac Asimov

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ABSTRACT

A series of polynuclear macrocyclic complexes has been prepared by the Schiff-base condensation of 1,5-diaminopentan-3-ol with 2,6-diformyl-4-methyl-R-phenol (where R = Me or tBu) in the presence of transition metal template ions. The (2 + 2) macrocyclic complexes, containing two or four metal ions, have been characterised by a variety of methods including microanalysis, infrared spectroscopy, cyclic voltammetry, E.I. and FAB mass spectrometry and X-ray crystallography.

When the template ion is copper, tetranuclear complexes are obtained. The structures of $[Cu_4(\mu_4\text{-}OH)\mathbf{L1}(CH_3CN)_3(ClO_4)_2]\cdot ClO_4\cdot H_2O$ and $[Cu_4(H_2LV5)(dfmp)_2Cl(H_2O)_2]\cdot BF_4$ have been determined; both complexes contain planar tetracopper cations with an exogenous hydroxo donor in the centre of the cavity, bound to all four copper ions. Under appropriate conditions the tetracopper complexes dimerise to form octacopper assemblies and the structure of one of these $[\{Cu_4(\mu_5\text{-}O)LV5(ClO_4)\}_2]\cdot(ClO_4)_2\cdot 4H_2O$ is reported. Ligand binding to the exposed faces of these arrays was investigated.

Tetranuclear cobalt complexes have also been prepared. The X-ray structure of $[Co_4(\mu_4\text{-}O)\mathbf{LV5}(CH_3COO)_4]Cl\cdot 3H_2O$ shows that, in contrast to the copper complexes, the cation is not planar and the central exogenous donor is an oxo rather than a hydroxo ligand. Tetracobalt complexes can be obtained at various oxidation levels between $Co(II)_4$ and $Co(III)_4$.

A series of dicobalt complexes has been synthesised. In contrast to the familiar Robson dinuclear complexes, the cobalt ions are not bridged by phenolate donors but are diagonally disposed in the cavity and bridged by two chloride ions. X-ray crystal structure determinations have been carried out on five of these complexes, each having a core structure of $[Co_2(H_4L)Cl_2]$. These complexes offer a potential route to the formation of tetranuclear complexes containing mixed metal ions.

Synthetic organic work directed towards the development of new ligands was also undertaken.

CHAPTER 1

THE PHENOL-CONTAINING SCHIFF BASE MACROCYCLES

Section one : Metal Complexes from Polynucleating Ligands

1 : THIS REVIEW

This review is in two parts. The first section provides an overview of the development of polynucleating Schiff base ligands in general. Because of the enormity of this subject the discussion has been restricted to transition metal Schiff base macrocyclic "bridging donor" complexes of the type M_xL in which X = 2-8, the ligand (L) contributes at least three nitrogen or oxygen donor atoms in the coordination sphere of each metal, and the metals are bound within a reasonably well-defined geometric relationship. Non-macrocyclic, pendant-arm and "isolated donor set" complexes along with those having other than nitrogen or oxygen donor atoms will not be discussed in detail here. However, ligands containing sulfur donors and some rare earth complexes will be alluded to.

In the second section the Schiff base complexes which have a phenol head unit are discussed. Ligands have been arranged according to the nature of their diamine precursors. Emphasis is placed on the synthesis and properties of complexes which incorporate two or more metal ions. The discussion focuses on properties of the ligands relating to the coordination geometry of the metal ions.

2 : INTRODUCTION

Since the early 1970's the potential importance, in catalytic processes, of molecules containing multimetal centres has been recognised and has consequently influenced the development of metal cluster chemistry. In traditional macrocycles an organic framework holds a number of metal ions via

coordination to sulphur, nitrogen or oxygen donors. This is in contrast to the strictly organometallic clusters in which metals are bonded to a molecular framework via carbon atoms. There is also a contrast in the oxidation states of the metals in these two systems, with the metals in the macrocyclic compounds usually being in medium to high oxidation states while those in organometallic clusters are usually in lower oxidation states. With the discovery of many proteins and enzymes requiring two or more metal ions for their activity, there was an early awareness that polymetallic complexes also played an important role in the area of bioinorganic catalysis. It was realised that the catalytic action of these compounds depended on finely balanced metal-metal interactions. Examples of molecules utilising such mechanisms are urease (a nickel metalloenzyme); the copper and zinc containing superoxide dismutase; the purple acid phosphatases which have two iron centres in their active sites; and the tetramanganese oxygen-evolving complex (OEC) of photosystem II[1-4]

A desire to "mimic" the active sites of these metallobiomolecules[5-20] has been one of the driving forces behind the development of the chemistry of macrocyclic binuclear and later polynuclear complexes. In addition, interest has been shown in polymetallic complexes for their potential in the binding and activation of small molecules[21,22] and in the investigation of the mutual influence of the metal centres on the electronic, magnetic, and redox properties of such systems.[21-24]

Designing polydentate ligands which are capable of fixing a number of metal ions in the appropriate juxtaposition to each other has been one approach to understanding the nature of these complicated intramolecular interactions. It was hoped that properties and characteristics of these complexes might lead to elucidation (and maybe mimicry) of the mechanisms by which the complicated biological polymetallic systems worked.

In her review of macrocyclic models for nonporphine metalloproteins M^{c}Kee[4] identifies the challenge of modeling such systems as that of accounting for their unique spectral or chemical properties in terms of the coordination chemistry of

the metalloprotein active site, as moderated by the protein environment. In synthesising model complexes the aim is to reproduce and understand the spectroscopic features and the function of the metalloprotein and then to duplicate its function in a low-molecular-weight complex of known structure.[25-27] In many cases the particular properties of these sites are attributable to unusual geometry or ligation at the active site.

Many of these unusual properties can be duplicated in macrocyclic systems. If the metal ion imposes its preferred geometry on the macrocyclic ligand then the complex is likely to have classical coordination properties; but if the ligand imposes some particular geometry or environment on the metal, then the possibility of unusual properties of some sort is introduced. In most cases some degree of compromise is reached between the preferred geometry of the macrocycle and that of the metal. Macrocyclic ligands are useful then, in designing systems which may be used to modify the properties of the metal ion by providing unusual donor sets, placing the metal ion in unusual geometries and controlling the environment about the metal ion.

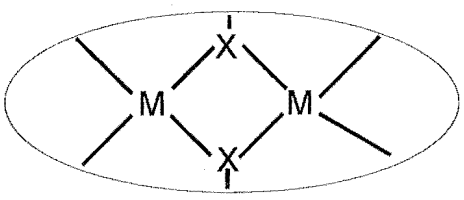
Just as in proteins, a metal ion in a macrocyclic complex will bind to donor atoms it would not normally favour, if these atoms are part of an imposed coordination environment and there are no alternative donors available. In this "host-guest" [28, 29] situation the binding is promoted by the presence of strongly binding donors that maintain the less-favoured donor within the coordination sphere. The fixed relative positions of the donors prevent side reactions which would occur if the ligands were independently labile. In imposing unusual coordination geometries, the concept of the protein (or macrocycle) as a host with a prearranged donor set is most relevant. The constrained geometry of the metalloprotein, or its macrocyclic analogue, is designed to disrupt the preferred geometry of the metal and so modify its properties. In this way factors such as coordinative unsaturation or metal-metal interactions can be controlled.

It must be noted that in these design strategies, a complex may mimic closely the structure and the spectroscopic properties of a metalloprotein active site

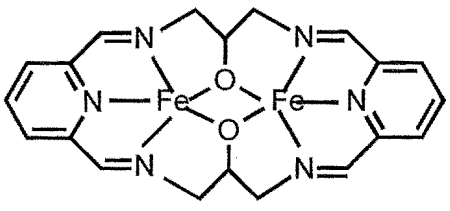
without reproducing its function. Alternatively, many excellent functional models are structurally quite distinctly different to the known active sites. In both cases, a good understanding of the factors which control the essential properties of the natural site is required.

Often, when local site geometry and metal ion spectroscopy appear to have been reproduced accurately, there are still effects not accounted for. Generally these are attributed to the influence of the "protein environment"; a factor which is much less easy to model. In metalloproteins characteristics such as access to the site, polarity, and a protic or nonprotic environment in the vicinity of the metal ion are controlled by nearby amino-acid residues and by the exposure of the site to the external solvent. Modeling these subtle effects can be achieved in a number of ways, such as the use of nonprotic solvents, and has led to the development of large macrocyclic ligands that wrap around the metal site[4].

The scope of the subject of this review is enormous and only the macrocycles having "bridging donor sets", i.e. those in which the metals share at least one macrocyclic donor atom, will be discussed. Many of the ligands in the bridging donor set class are Schiff base complexes resulting from the condensation reactions of dicarbonyl species with diamines. The "head units" of these macrocycles are commonly dicarbonyl heterocycles or derivatives of either 2,6-disubstituted phenols or 1,3,5-tri-ketonates in which the phenolic oxygen or the central keto oxygen acts as a bridging donor atom. The diamine side chains range from simple alkane types to those incorporating amine and alcohol functional groups. The binucleating ligands include a wide variety of macrocyclic and pendant-arm type complexes.



a



b : e.g $[Fe_2^{III}(LVD)(H_2O)_4]^{4+}$

Figure 1

Within the "bridging donor set" group, the macrocyclic complexes can be further differentiated into those in which the metals are bridged by both the donor groups in the head units and in the lateral arms (Figs. 1a & b)[30] and those in which the metals are held at the separate ends of the macrocycle and are not bridged by lateral arm donor groups (Fig. 2a). The metals may (Fig. 2b)[31] or may not (Fig. 2c) have contact, via other groups, with the metal(s) held at the other end of the cavity.[32]

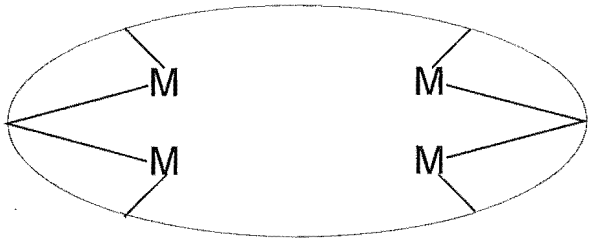


Figure 2a

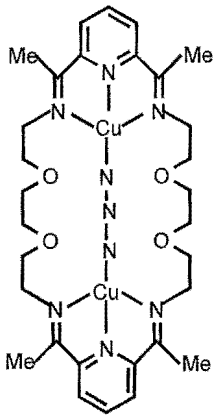


Figure 2b

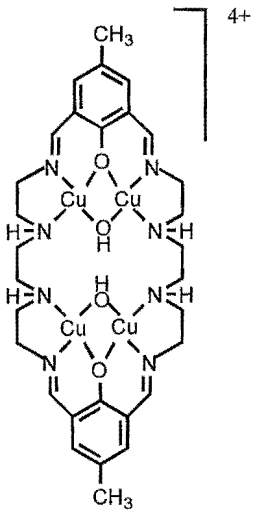
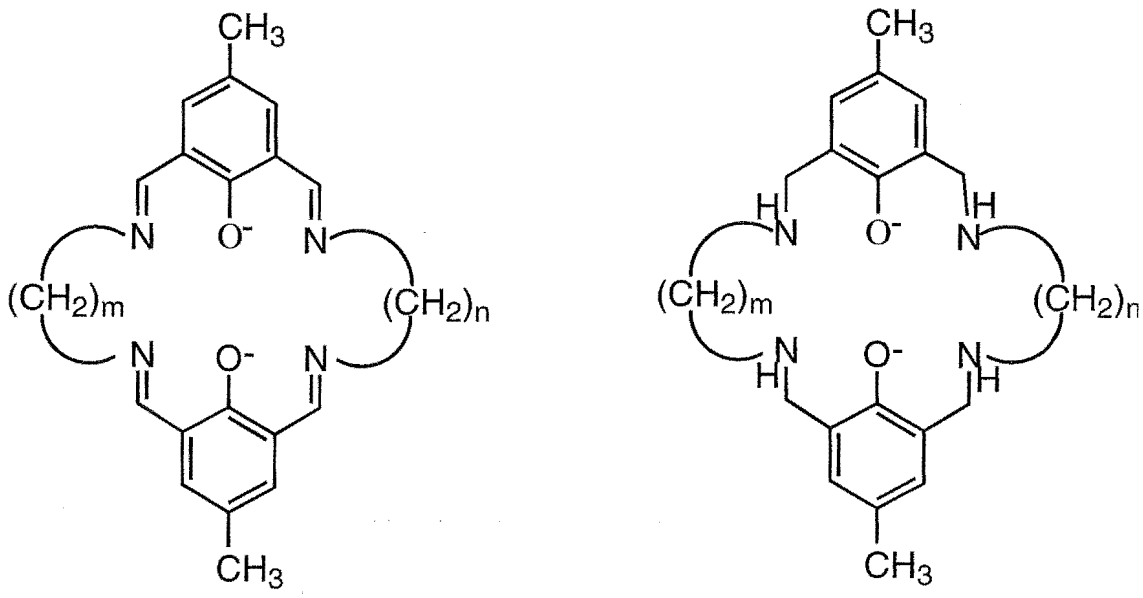


Figure 2c

In 1970 Robson and Pilkington[33] published the first example of a binucleating Schiff-base macrocyclic complex based on 2,6-diformyl-4-methylphenol (dfmp) with 1,3-diaminopropane. The subsequent exploitation of phenol-containing systems has been extensive and since that time many other "Robson" type macrocycles have been synthesised. The vast majority are binucleating macrocycles of Type I (imine containing) (Fig. 3) with various numbers(*m,n*) of CH_2 groups in the lateral chains, and in which two metal ions are bound in the cavity and are bridged by the two deprotonated phenolate groups. In most cases the macrocycle is symmetric but asymmetric cases where ($m \neq n$) are

known.[9,33-35] The range of these alkane chain macrocycles includes types with (*m,n*) = (2,2), (2,3) (2,4) (2,5), (3,2), (3,3), and (3,4). The alkane lateral chains have been modified to include ether,[36-38] amine,[32,37,39-41] alcohol,[42-49] sulphur,[50,51] and even benzyl[34,52,53] variations.



I II

Figure 3 : Type I (imine containing) and Type II (amine containing) Robson Ligands.

In 1977 Nelson and his co-workers investigated the coordination chemistry of some pentadentate Schiff base macrocycles.[54] They found that in the presence of lead(II) cations a condensation occurred between 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine to give, not the anticipated mononuclear complex of the pentadentate macrocycle (Fig. 4a), but a dinuclear decadentate macrocyclic ligand (Fig. 4b).[55] This discovery initiated a study of tetraimine Schiff base macrocyclic complexes derived from heterocyclic dicarbonyl head-units.[22,56,57]

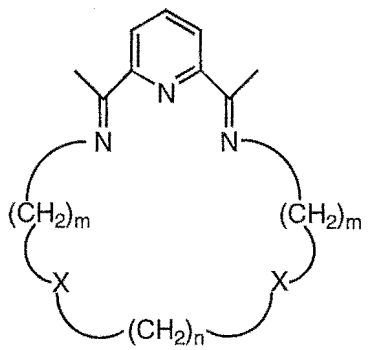


Figure 4a

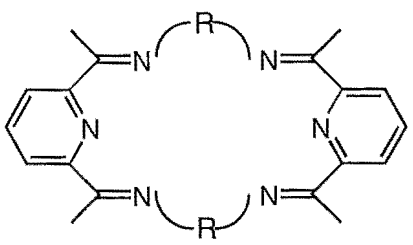


Figure 4b

Typically, dicarbonyl units of the type shown in Figure 5 have been used with a very wide range of diamines. The development of this area of macrocyclic chemistry was facilitated by the use of alkaline earth and main group elements as templating ions and by transmetallation reactions to give transition metal complexes which were otherwise inaccessible.

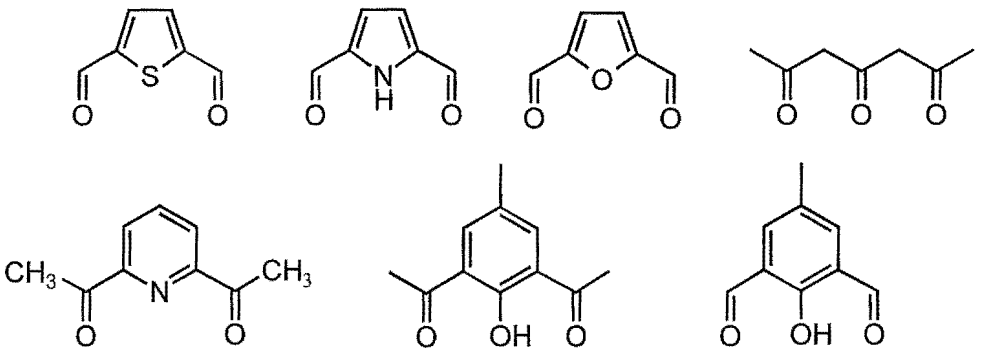


Figure 5 : Representative head units.

The progression to expanded macrocycles, able to accommodate more than two metal ions, has been accomplished by a number of groups. M°Kee's approach to these syntheses was based on incorporating alcohol bridging groups into the diamine synthons of the macrocycles.[5,14,43-47] The template synthesis, using 2,6-diacetylpyridine and 1,3-diaminopropan-2-ol, had produced a barium complex of the [2 +2] Schiff base macrocycle **LD1** (Fig. 6) which had subsequently been transmetallated to form a mono-bridged binuclear copper(II) complex.

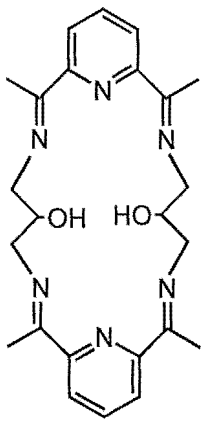
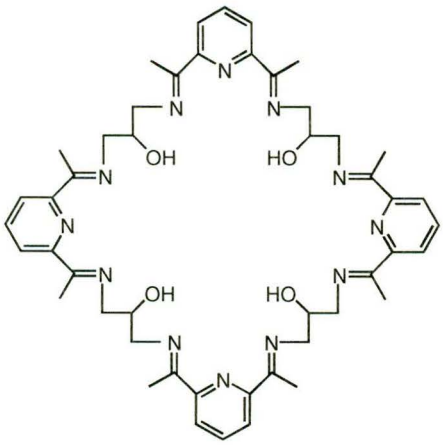


Figure 6 : Ligand LD1

This procedure, using Ba^{2+} followed by $Mn(ClO_4)_2 \cdot 6H_2O$, produced not the expected binuclear product but a complex which X-ray analysis showed to be $[Mn_4(\mathbf{LD2})](ClO_4)_4$. That the [4 + 4] macrocycle (Fig. 7a) formed after manganese transmetallation of the barium [2 + 2] moiety was confirmed by californium-252 plasma desorption mass spectrometry. The macrocycle was folded in such a way that the four alkoxide oxygen atoms capped the faces of a tetrahedral Mn_4 cluster resulting in a cubane-type core (Fig. 7b).



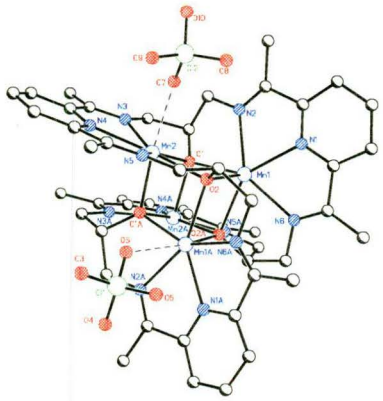


Figure 7a : Ligand LD2 **7b : Perspective diagram of $[Mn_4(LD2)] \cdot (ClO_4)_2$**

The size of the Ba^{2+} ion indicated this same reaction should be suitable for lanthanide ions and this has been carried out with the products variously reported by Sakamoto[58] as [2 +2] or Fenton as [3 +3][59] condensations; the latter based on interpretation of elemental analyses and NMR spectroscopy. Aspinall[60] showed, by X-ray analysis, that when the reaction was carried out in the presence of $La(NO_3)_3$ the product was in fact the [3 +3] complex $[La_3\mathbf{LU}(\mu_3\text{-}OH)(OH)(NO_3)_4] \cdot 7H_2O$ (Fig. 8).

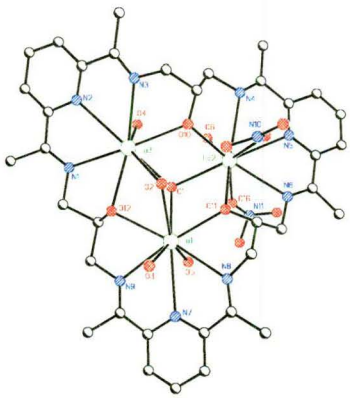


Figure 8 : The structure of the La_3LU complex (some H_2O and NO_3^- groups omitted)

By enlarging the alcohol-containing diamine to a five carbon system a macrocycle large enough to accommodate four metal ions was synthesised by M^{c}Kee's group.[44] The ligand **LV5t** (Fig. 9a) was formed by the condensation of 2,6-diformyl 4-*tert*-butylphenol with 1,5-diamino-3-pentanol. Robson also reported tetranuclear complexes[61,62] of the ligand **LAmP** (Fig. 9b) formed from 2,6-bis(aminomethyl)-4-methylphenol and 2,6-diformyl-4-methylphenol.*

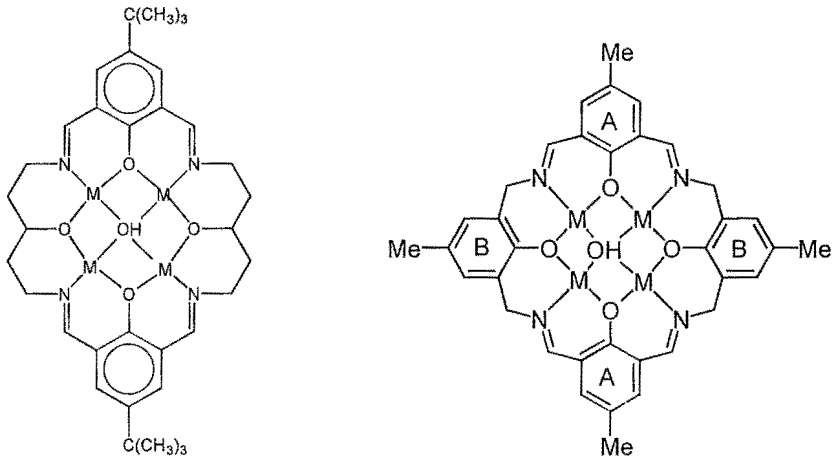


Figure 9 : The ligands LV5 (a) and LAmp (b)

Further functionalisation of the lateral chains to create bibracchial variations has been exploited. Fenton theorised that suitable modification of the pendant arms could lead to the synthesis of trinuclear metal complexes.[63] This was accomplished by modification of the bibracchial tetraimine Schiff base macrocycles **LFb** derived from the silver templated cyclocondensation of 2,6-diacetylpyridine and tris(2-aminoethyl)amine. Mononuclear barium and dinuclear silver complexes were made using the variations of **LFb** shown in Figure 11.

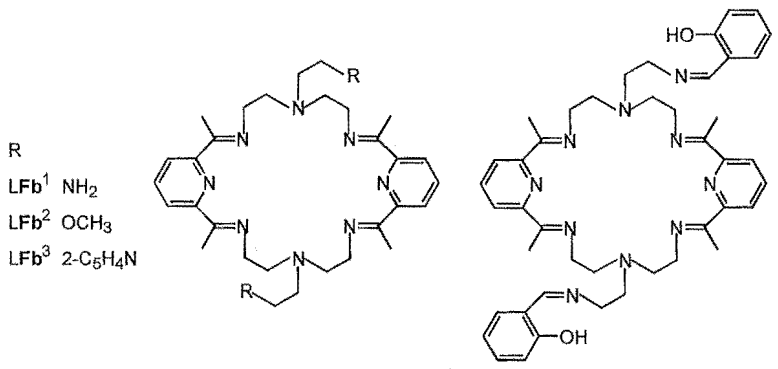


Figure 11 : Fenton's bibrachial ligands

* **LV5t** and **LAmP** are discussed in detail in Sections 1·3·2 and 1·3·3 respectively.

Functionalisation of the pendant arms of the disilver **LFb**[1] complex with salicylaldehyde followed by transmetallation with Cu(II) was carried out to form the trinuclear copper(II) complex $[Cu_3(\mathbf{LFb^4})(OH)](ClO_4)_3{\cdot}2H_2O$ (Fig. 12).

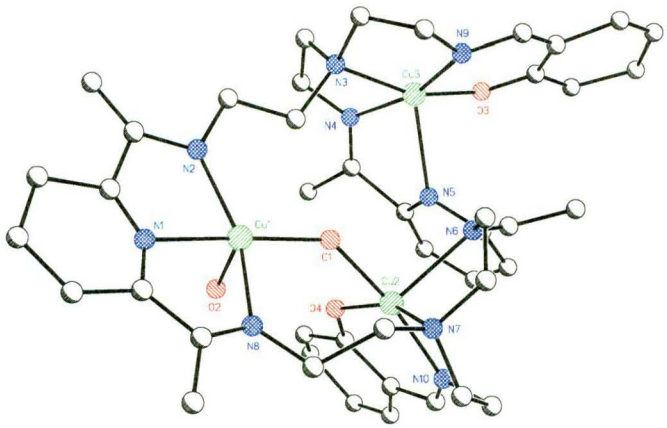


Figure 12 : The $[Cu_3(LFb^4)(OH)]^{3+}$ cation

2.1 : Reduction of Imine Systems

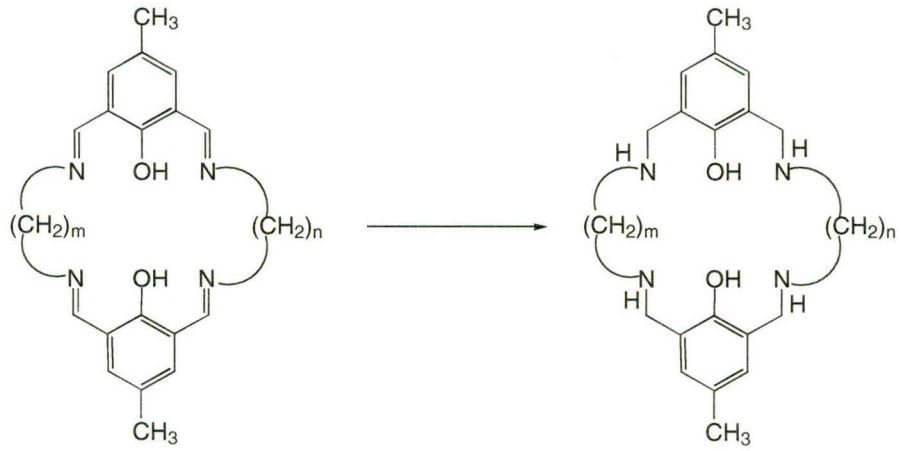


Figure 13

The imine linkages in all of the macrocyclic systems can be reduced to the corresponding amines. In the late 1980's Mandal *et al.* synthesised a Type II (Fig. 13) macrocycle with $m = n = 3$ and studied its dinuclear copper(II) complexes.[64,65] Since then it has been of interest to many research groups to compare the properties of the Type I (imino) systems to their Type II (amino) analogues and a large number of saturated and partially saturated complexes

have been added to the series. Study of partially saturated complexes (and those with differing lateral chains) has been motivated by interest in macrocycles which contain dissimilar coordinating sites. Most often the reduction is effected chemically with sodium borohydride in methanol[64], or electrochemically[66]. Often, by various means, the reduced ligands are released from their metal ions giving routes to the free ligand. An advantage of the free saturated ligands over their imine precursors is their resistance to hydrolytic degradation.

3 : SYNTHESIS OF THE MACROCYCLES

3·1 : Synthetic Approaches

There are two major methods of synthesising the Schiff base macrocycles. In the first, i.e. the "direct" or non-template synthesis, the procedure is independent of any directing influence of the metal ion and the cyclisation is the result of an organic reaction. In the second method the metal ion to be incorporated into the complex acts as a "template" around which the ligand is cyclised.

Vigato and Fenton stated[67] that a macrocyclic complex is ideally formed by adding the required metal ion or ions to a preformed ligand. Fenton[68] confirmed that this is because once the ligand is established this method should maximise the formation of the desired complex. The metal template route (refer Section 3·2) is not accessible to all metals, so transmetallation may be necessary. In attempting transmetallation a number of difficulties can be encountered. Reductive elimination can remove the original metal but modify the ligand, or precipitating agents can hydrate or hydrolyse the ligand.

However, in the formation of a macrocyclic ligand, a major problem to be overcome is the occurrence of polymerisation instead of the desired cyclisation. Generally, equimolar amounts of the two reactants (which incorporate moieties required in the final structure) are allowed to react in such a way that a condensation occurs. The probability of the partly condensed intermediate

reacting with itself in what Lindoy[69] describes as a "head-to-tail" manner is greatly increased if the reaction is carried out at very high dilution. This dilution can be achieved by adding metered quantities of the reactants into the solvent at an extremely slow rate so that the concentrations of the unreacted starting materials, at any given time, are very small. In some reactions, which had either very low yields or produced other than the desired products, the yield of the target molecule was much increased by using high-dilution techniques. For example in the reaction illustrated in Figure 14 changing the dilution of the reaction improved the yield from 7·5 to 55%.[70,71]

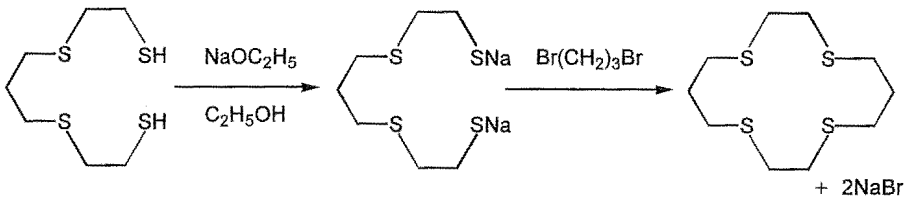


Figure 14

Typically for crown ethers, the cyclisation involves a Williamson synthesis. The Williamson synthesis involves the nucleophilic displacement of a halide or tosylate group by an alkoxide or phenoxide ion. In other reactions the addition of tosyl groups to the reactants has meant that increased yields have been achieved at quite moderate dilutions. It is thought that by reducing the number of conformers available to both the reactants and the intermediates, the reactants are pushed to cyclisation rather than polymerisation[67].

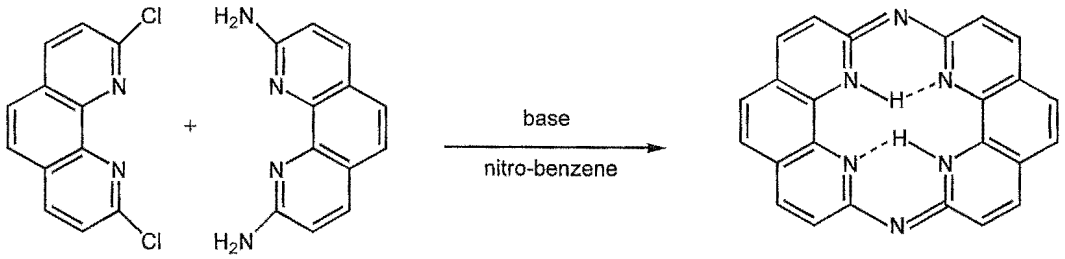


Figure 15

Yields at other than high dilution can also be improved if intramolecular hydrogen bonding occurs as the macrocycle forms. This was seen in a ligand series containing anilo-nitrogen atoms[72] and between the heterocyclic nitrogen

atoms in a phenanthroline containing macrocycle (Fig. 15).[73] The rigidity of the phenanthroline precursors could also favour cyclisation occurring as the introduction of rigid groups, to restrict rotation in the open-chain precursors, is another way of facilitating cyclisation. The length of the chain also influences the rate at which cyclisation will occur.

Overall, it appears that, for macrocycles to be formed in high yield without the use of a templating ion or employing high dilution techniques, there has to be something special about the circumstances, as shown in the examples just discussed.

The formation of Schiff base macrocycles is greatly influenced by the both the nature and the purity of the solvent employed in the reaction. For example, in the reaction between 2,6-diformylpyridine and 1,2-bis(1-aminophenoxy)- ethane the expected [2 + 2**LP1**] product resulted, if the reaction was carried out in "dry" benzene, but in "wet" benzene the macrobicyclic aminal **LP2** formed (Fig. 16)[74].

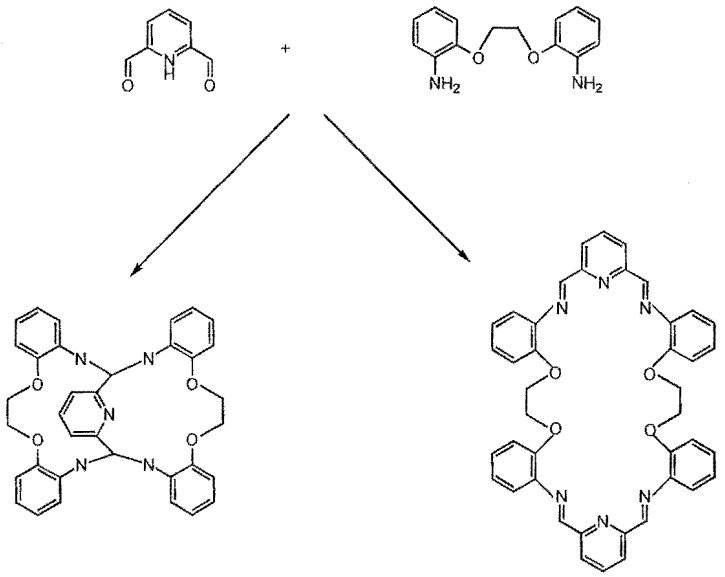


Figure 16 **LP2** **LP1**

Many macrocyclic imine systems are subject to hydrolysis if water is present in the solvent system. This does not seem to be a major problem with the phenol systems.

Although open and podal Schiff base ligands are frequently formed by direct condensation methods it is uncommon for the Schiff base macrocycles to be formed this way. Only [1 + 1] and [2 + 2] direct condensations are known and representative examples can be found in references 75 - 79.

Jane Nelson and Jean-Marie Lehn independently pioneered the synthesis of potentially dinucleating macrobicyclic ligands in [2 + 3] one-step direct condensation reactions. The preparation of these ligands is represented schematically below (Fig. 17).[80-84]

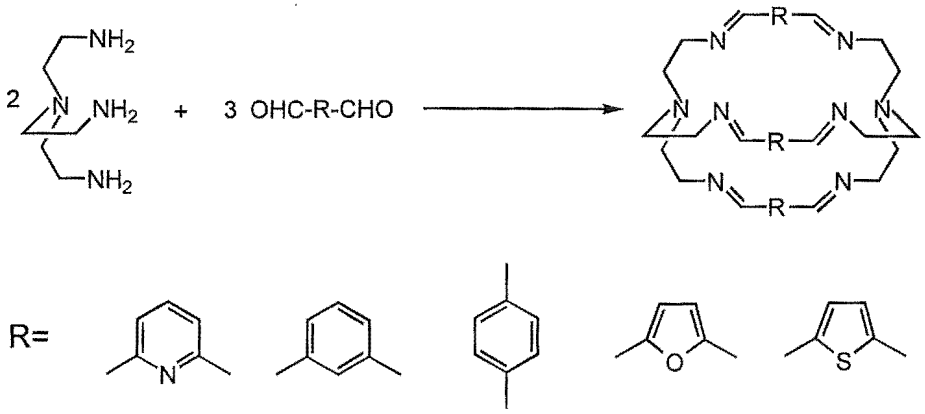


Figure 17

It must also be noted that in many non-template procedures, the presence of Lewis acids (such as K^+, Na^+, BF_3, or $B(OH)_3$) enhanced the cyclisation process. They are implicated in forming stable intermediates* such as that shown in Figure 18 and so it would seem that these syntheses are sometimes a balance between template and non-template routes.[85]

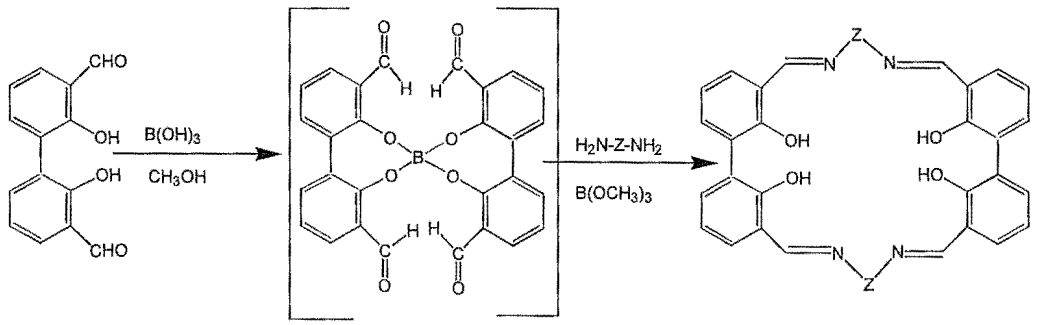


Figure 18

* This intermediate has not been isolated, but boron was essential for a good yield of the macrocycle.

3·2 : Metal Template Procedures

The presence of a metal ion in the cyclisation reaction often markedly increases the yield of the macrocyclic complex in what has been termed the metal-template effect. The template ion which is most likely to be an alkaline earth metal, transition metal, lanthanide or actinide, promotes the cyclisation by directing the course of the reaction.

This effect has been recognised since 1928 after a cyclic Fe(II) phthalocyanine complex was formed as an unexpected product when the preparation of phthalimide, from phthalic anhydride and ammonia, was carried out in an iron vessel. This discovery led to the use of finely divided metals, or metal hydrides, oxides, or chlorides, to promote these types of reactions.

However, it wasn't until 1961 when Curtis[86] treated $Ni(en)_3(ClO_4)_2$ with acetone (en = $NH_2CH_2CH_2NH_2$) to yield a tetraazamacrocyclic complex that the synthesis of other sorts of cyclic systems developed. This was the first example of a template synthesis on a transition metal and from this developed the enormous range of such reactions now known.

Busch has postulated[87] that, in metal template procedures, the template ion promotes formation of the desired product in one of two major ways. It may shift the position of an equilibrium between the starting materials and the cyclic product by sequestering the latter, as the metal complex, from the mixture in a process known as the thermodynamic template effect. In the other process, called the kinetic template effect, the metal ion is thought to sterically influence the course of the reaction in such a way that the cyclic product is favoured. However, it is generally accepted that, in most situations, the role of the metal ion is more complicated than these processes suggest and could involve both effects as well as other little-understood mechanisms.

The formation of the Schiff base macrocycles is most often effected by the template procedure.[8,9,24] Equimolar amounts of the organic precursors react in

the presence of a transition metal salt in alcoholic solution. In the mid 1970's, groups in Belfast[55,88,89] and Sheffield[89-91] pioneered the use of alkaline earth metals and main group elements such as tin and lead, as templating metals.

It would appear that the two most significant controlling factors in these reactions are the cationic radius and the nature of the donor atom. Both the success of the synthesis and the geometry of the resulting complex are dependent on the compatibility of the macrocyclic "hole" and the radius of the templating cation. For example, for the ligand system shown in Fig. 19 it appears that cations of radii less than ~ 0·8 Å will not generate macrocyclic complexes. Neither Cu(II) nor Ni(II) act as templates for this group of macrocycles yet are commonly used to template tetradentate 'N_4' macrocycles[92] A probable explanation for this is the preference of these cations for stereochemistries in which the metal has tetragonal geometry rather than being pentagonally based.

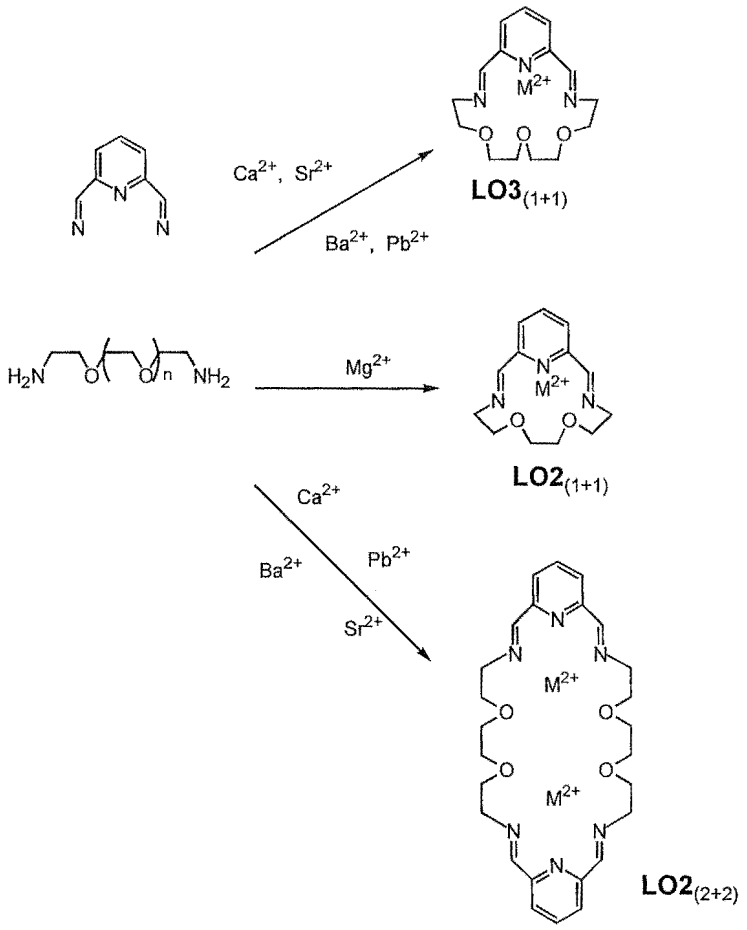


Figure 19 : Schiff base macrocyclic synthesis in the presence of non-transition metal templates.

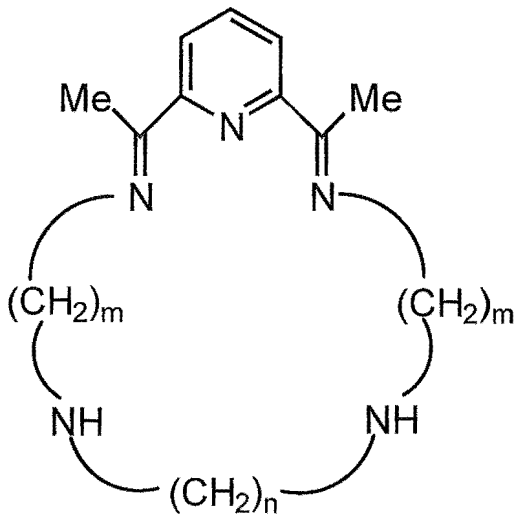
Of the alkaline earth metals, only Mg^{2+} (r = 0·74 Å)[89] acts as a template for the pentadentate [1+1] macrocycle **LO2**$_{(1+1)}$, (Fig. 19) but fails to generate the hexadentate **LO3**$_{(1+1)}$ (Fig.19) which is easily synthesised if Sr^{2+} (r = 1·16 Å), Ba^{2+} (r = 1·36 Å), Ag^{+} (r = 1·15 Å), Pb^{2+} (r = 1·18 Å) are used as the templating ions.[22,55,93] The influence of the cation size is further emphasised in noting that if these same ions are used with the shorter lateral chain, [2+2] condensations occur (Fig. 19).[94-96]

The type of donor atom is as important as the cavity size. In the same example, (Fig. 19) the use of Pb^{2+} leads to the formation of **LO2**$_{(2+2)}$ but if it is used with the all-nitrogen system, -$(CH_2)_2$-NH-$(CH_2)_2$-NH-$(CH_2)_2$-, the [1+1] product **LN2**$_{(1+1)}$ is produced. The Pb^{2+} lies significantly closer to the nitrogen donors than it does to the oxygen donors in the complex Pb_2**LO2**$_{(2+2)}(SCN)_4$[55] or in a related 'N_3O_3' macrocycle.[90] This suggests that the formation of the macrocycle is influenced by the strength of the interaction between the metal and the donor atom. If this interaction is strong, then the terminal NH_2 and the C=O groups of the likely intermediate can be brought into the appropriate *cis*-alignment required for the [1+1] product; but with weakly coordinating donors these terminal units are less likely to be in close proximity and a [2+2] product results.

3·3 : Transmetallation

Many Schiff base macrocycles which can only be prepared by template methods cannot be released from their complexes as free ligands. These Schiff bases are only stable when coordinated and attempts to isolate the free ligand results in ligand hydrolysis. There would be severe limitations in using these Schiff bases to form complexes if it weren't for the fact that for most of them the templating ion can be replaced in the complex with another metal ion. The replacement metal ion may be one which could not be used for the original synthesis. Alkaline earth metal and lead(II) ions have been found to be unusually kinetically labile to this "transmetallation" process and are readily replaced by transition or other metal ions capable of forming stronger bonds

with the ligand donor atoms.[22,54,92,96,97] There are many ways in which this property can be utilised. Metal ions can be introduced into systems with stereochemistries usually unfavoured by them. An example of this is the transmetallation of Cu(II) into the diacetylpyridine based complexes[54] shown in Figure 20, thus forming complexes unable to be formed using Cu(II) ions directly as template. Another important aspect of transmetallation is that a single large metal ion (e.g. Ba(II), in a [2 + 2] macrocycle) can often be replaced with two smaller ions (e.g. Cu(II)) to form binuclear complexes. Even metal ions which are quite strongly bound to the ligand can be displaced if the replacement is assisted by the use of an anion which forms an insoluble salt with the template metal ion. Complexes containing Ag(I) on treatment with a Cu(II) halide will form Cu(II) complexes after the silver halide has precipitated.[97]

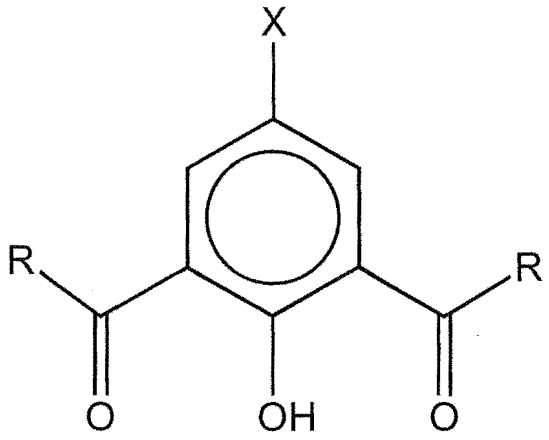


(222 - N_5) m = n = 2
(232 - N_5) m = 2, n = 3
(323 - N_5) m = 3, m = 2

Figure 20

SECTION TWO : THE PHENOL BASED LIGANDS

1. : INTRODUCTION



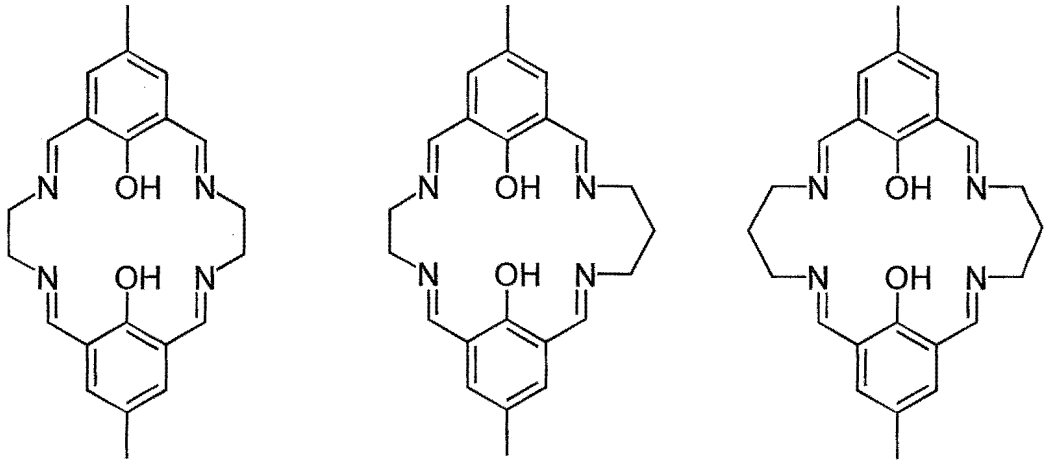
R = H, CH_3, $CH_2CH_2CH_3$, C_6H_6, OH.

X = H, CH_3, $C(CH_3)_3$, NO_2, Cl, OH, Br, CF_3.

Figure 21 : The Phenol Head Unit

Derivatives (only some representative references are given here) of 2,6-diformyl-4-methylphenol (Fig. 21) have been used extensively in the formation of binuclear metal complexes,[98-107] macrocyclic binuclear metal complexes[35,108-110] and more recently macrobicyclic complexes.[111] Variations of X have included H,[112,113] CH_3,[8,43,114,115] $C(CH_3)_3$,[46,52] Cl,[116,117] CF_3,[118] NO_2,[119] Br,[120] and OH.[121] Only podand complexes of the latter three have been reported and these will not be discussed here. Although diformylphenol derivatives are most frequently used as the head unit in this class of macrocycles, the diacetyl variation is quite common and investigations in which the R group has been systematically changed have also been carried out. These changes have included R = methyl, n-propyl, phenyl and hydroxy, and R may or may not be the same as R'.[114,122,123] It is more difficult to close the macrocycles when acetyl derivatives are used. Fenton has theorised[107] that this is probably due to the methyl groups present in the acetyl complexes inhibiting the reaction of the carbonyl groups (positive inductive effect) and having greater steric requirements than the formyl group. Relatively few acetyl containing macrocycles have been reported.

1·1 : Synthesis



H_2L2-2 H_2L2-3 H_2L3-3

Figure 22

The Robson macrocycles $H_2L(m,n)$ **L2-2**, **L2-3**, and **L3-3**,* (Fig. 22) are condensation products of 2,6-diformyl-4-methylphenol and either 1,2-diaminoethane or 1,3-diaminopropane. These comprise the most studied class of phenol-containing macrocycles, having been used extensively in the study of homo- and heterobinuclear and mixed valence complexes.[124-126] Complexes with the same lateral chains ($m = n$) are synthesised in a one pot reaction using a suitable metal ion template and, in fact, all attempts to produce metal-free neutral ligands have failed under all conditions tried.[8] Although the alkali metals have been used extensively as templating ions in other systems they had rarely been used to synthesise Schiff base macrocycles. Recently, Fenton *et. al.*[127] have used the sodium ion to synthesise disodium complexes of a Robson ligand. This complex is used as a "free ligand" and readily undergoes transmetallation by transition metals to form dinuclear macrocyclic Schiff base complexes. Unsymmetrical macrocycles with different lateral chains cannot be prepared by the one-pot method; the best way being a sequential route (Fig. 23) in which a mononuclear complex, is first formed (with or without template techniques); treatment with a second equivalent of the diamine yields the mononuclear macrocyclic complex, and may be followed by the introduction of

* The ligand labelling scheme is based on the number of carbons in the lateral chains.

a second metal ion.[124] This method makes possible the mixed diamine and/or diimine derivative **L2-3**.

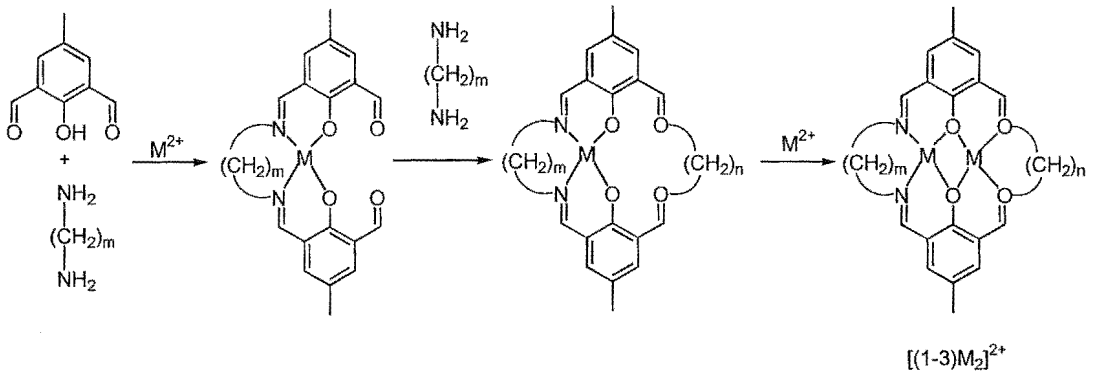


Figure 23

Usually, first row transition metal ions were used in the template syntheses of **L3-3** but recently Mandal[128] reported the $[Pb_2(\mathbf{L3\text{-}3})(NO_3)_2]\cdot 4H_2O$ and Okawa[129] $[Pb_2(\mathbf{L3\text{-}3})(ClO_4)_2]$ complexes (and in the case of the latter the crystal structure) of this ligand. M^{c}Kee[42] had also reported both the crystal structure of the mono-lead $[Pb(H_4\mathbf{LV3})]\cdot(ClO_4)_2$ and the $[Pb_2(H_2\mathbf{LV3})]\cdot(ClO_4)_2$complexes of **LV3** (the alcohol containing analogue of **L3-3**) (Fig. 24). M^{c}Kee's group also isolated the $[H_6\mathbf{LV3}(H_2O)_2][ClO_4]_2$, the diaquo complex of the perchlorate salt of the **LV3** ligand system; this had potential use in the formation of transition-metal complexes of **LV3**. The structure of these ligands is discussed in more detail in Section 1·3·1.

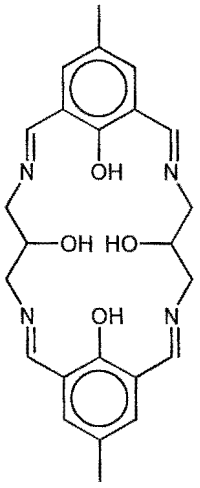


Figure 24

Schröder[83] acknowledged the potential of the preformed ligand by using it to develop routes to the platinum-metal complexes of **L3-3**. His strategy was to

first synthesise the protonated H_4**L3-3**$(PF_6)_2$ or H_4**L3-3**$(BF_4)_2$ species and insert platinum(II), palladium(II), or rhodium(II) into it. These protonated ligands adopt folded conformations with the two phenyl rings involved in inter- and intra-molecular (Fig. 25) stacking interactions. This conformation was not unknown having been reported earlier by M^{c}Kee[42] in $[H_6$**LV3**$(H_2O)_2][ClO_4]_2$ and by Fenton[130] in a mononuclear barium(II) complex of **LV3**. In contrast the crystal structure of the platinum-metallated complex showed it to be planar as expected.

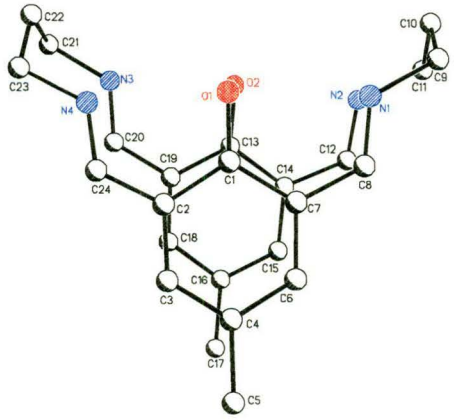
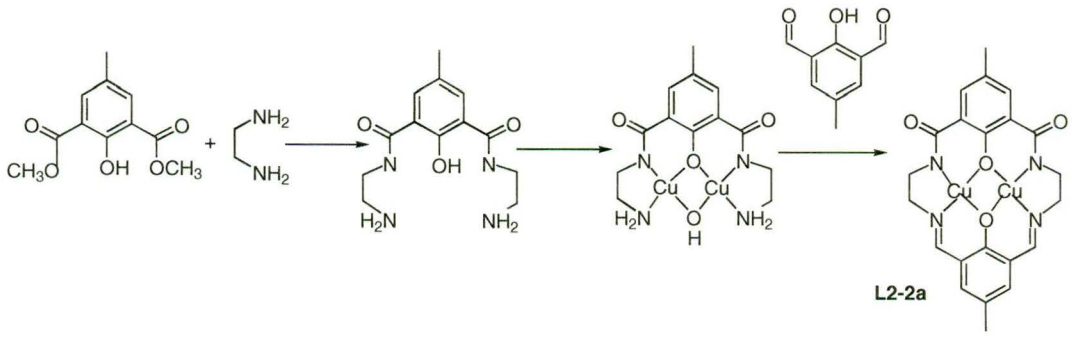


Figure 25 : The $[H_4$L3-3$]^{2+}$ cation showing its folded nature

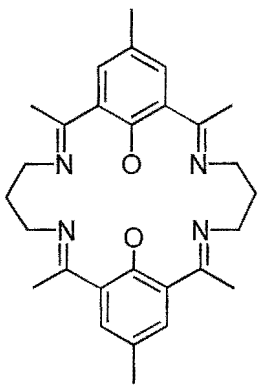
The unsymmetrical Schiff base macrocycle[23] **L2-2a*** derived from 2,6-diformyl - 4-methylphenol, an alkyldiamine, and 2,6-dicarboxylato-4-methylphenol (1:2:1) is a diimine-diamide "hybrid". The diamido linkages[23] were prepared first by treating 2,6-dicarboxylato-4-methylphenol with ethylenediamine and after formation of the binuclear copper complex , the 2,6-diformyl-4-methyl-phenol was added to complete the macrocycle (Scheme 1).



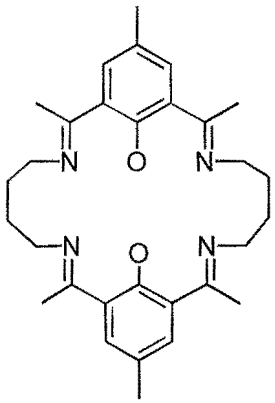
Scheme 1

* **L2-2a**- subscript **a** denotes acetyl analogue of the diformyl headunit.

Copper and nickel complexes **L3-3a** and **L4-4a** (Fig. 26) based on the diketo analogues of 2,6-diformyl-4-methylphenol, were synthesised by the template procedure.[131]



L3-3a



L4-4a

Figure 26

Nag *et. al.*[122,128] synthesised a series of dicopper(II) complexes of **L3-3** using the variations shown in Fig. 27.

L3-3 $R = R^1 = R^2 = R^3 = H$
L3-3a $R = R^1 = R^2 = R^3 = Me$
L3-3b $R = R^1 = R^2 = R^3 = Pr^n$
L3-3c $R = R^1 = R^2 = R^3 = Ph$
L3-3d $R = R^2 = Me$, $R^1 = R^3 = Ph$
L3-3e $R = R^1 = H$, $R = R^3 = Me$
L3-3f $R = R^1 = H$, $R^2 = Me$, $R^3 = Ph$
L3-3g $R = R^1 = R^2 = Me$, $R^3 = Ph$
L3-3h $R = R^1 = Me$, $R^2 = R^3 = Ph$

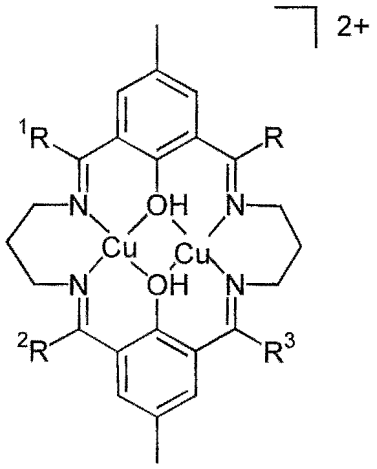


Figure 27 : Variations of L3-3

Synthesis was by two methods; either the template condensation of bis(aminopropane)-copper(II) perchlorate with the phenol or by reacting the dicopper(II)-diphenol perchlorate complex with 1,3-diaminopropane, both yielded 80% or better of the products.[122,128] An interesting development in the study[114] of this series was the discovery that if a dilute aqueous or aqueous-methanol solution containing the copper(II) perchlorate salt, the appropriate phenol (deprotonated with NaOH) and 1,3-diaminopropane were boiled for several hours hydroxo-bridged acyclic copper complexes of the type shown in

Fig. 28 were obtained as the major products and Cu_2L was formed only in small quantities.

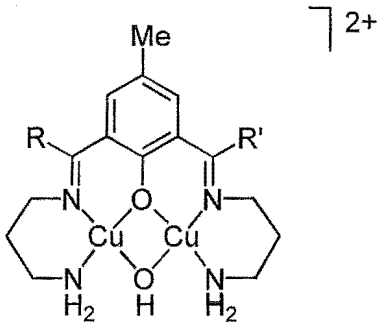


Figure 28

This discovery led to the synthesis of a range of complexes of podand ligands and also opened up a new route to unsymmetrical macrocyclic complexes as shown in Figure 29.

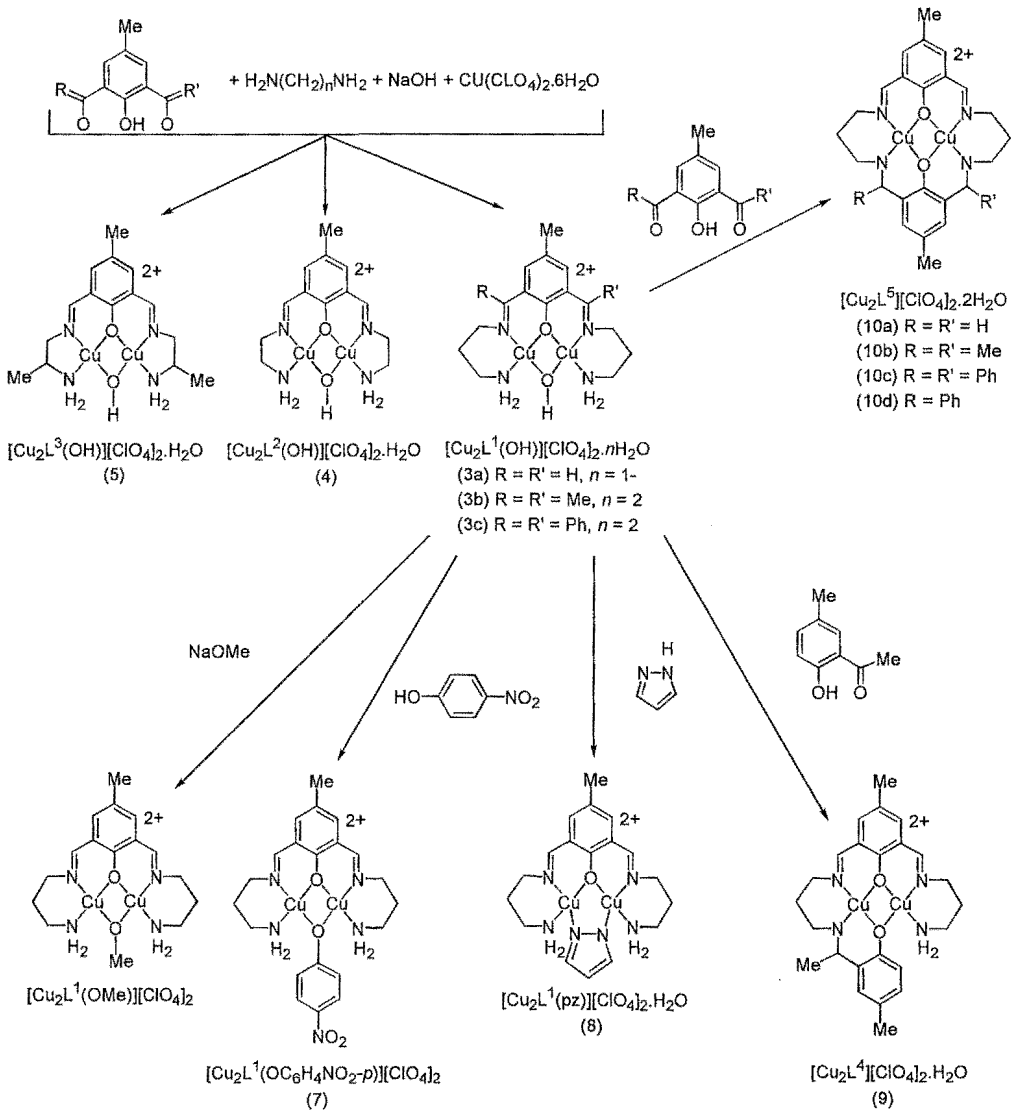
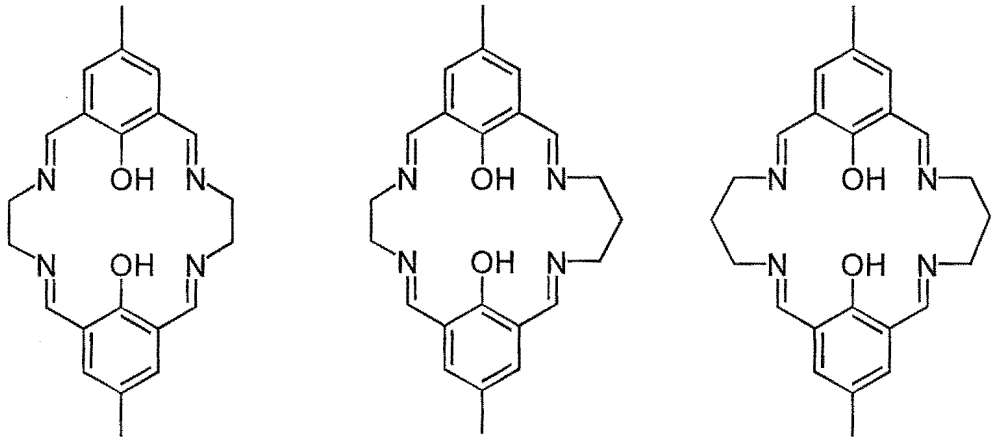


Figure 29

1.2 : Diaminoalkane Lateral Chains



H_2**L2-2** H_2**L2-3** H_2**L3-3**

Figure 30

The Robson macrocycles (Fig. 30) are probably the most studied of the Schiff base systems and many complexes of **L3-3** have been fully characterised. Pilkington and Robson[8] prepared a series of such complexes using Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. Square pyramidal geometry was assigned to the metals in the Cu_2, Ni_2, Co_2, and Fe_2 complexes based on the d-d transitions observed (Table 1). The apical coordination sites were occupied by anions or solvate molecules. For the Co_2 and the Ni_2 complexes the electronic data were consistent with both calculated and experimentally derived spectra for square pyramidal (not square planar) geometry and differed from those of complexes known to have octahedral and tetrahedral geometry. The magnetic properties did not support these metals having square planar geometry as they were both observed to have high spin configurations and all known examples of square planar geometry for these metals were diamagnetic or low-spin respectively. Conductance data and electronic spectral changes upon dissolution of the solid complexes in coordinating solvents further supported the assignment of the square pyramidal geometry.

This square pyramidal assignment was further confirmed in the Cu_2 and Co_2 cases, by X-ray crystallography. In the $[Cu_2(\mathbf{L3\text{-}3})Cl_2]\cdot H_2O$ chloride ions occupy the fifth apical sites with these sites being on opposite sides of the plane of the macrocycle as illustrated in Fig. 31.[125] The crystal structure showed that each

Co(II) ion was in an identical pseudo-square-pyramidal environment. The methanol molecule is disordered and partially occupies the sixth coordination site of each cobalt, with a long bond of 2·503(9) Å between the Co and the MeOH oxygen atom.

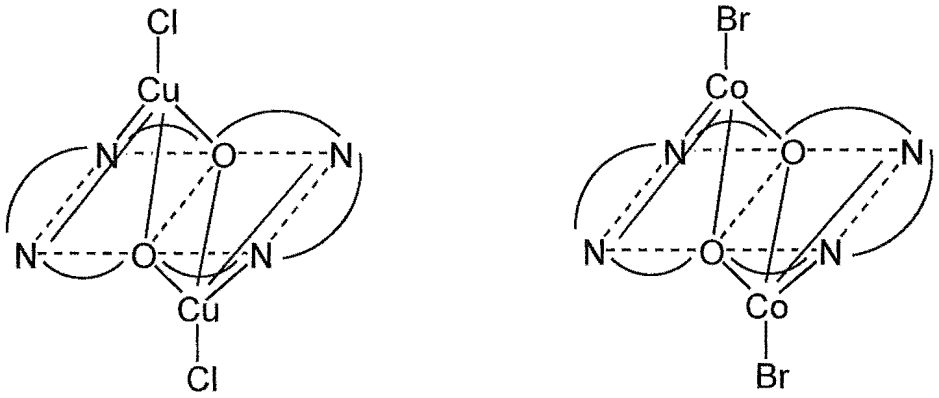


Figure 31

Table 1 :. Electronic Spectra for Compounds of L2-2, L2-3 and L3-3.[24]

Compound	Phase	Band position, cm^{-1}
$[Fe_2(\mathbf{L3\text{-}3})Cl_2]\cdot 2CH_3OH$	solid	8300
$[Co_2(\mathbf{L3\text{-}3})Cl_2]\cdot 2CH_3OH$	solid	17500(sh), 14300(sh), 9900
$[Ni_2(\mathbf{L3\text{-}3})Cl_2]\cdot 2H_2O$	solid	21000(sh), 17100, 10000(sh), 7500
	sol'n (H_2O)	22000(sh), 17800, 13600, 12800, 10000(sh), 8400
$[Cu_2(\mathbf{L3\text{-}3})Cl_2]\cdot 6H_2O$	solid	15000(asym)
	sol'n (H_2O)	16500, 14300(sh)
$[Cu_2(\mathbf{L3\text{-}3})(ClO_4)_2]\cdot 2H_2O$	solid	16100(asym)
	sol'n (H_2O)	16500, 14300(sh)
$[Cu_2(\mathbf{L3\text{-}3})SO_4]\cdot 2H_2O$[a]	solid	15000(asym)
	sol'n (H_2O)	16500, 14300(sh)
$Cu_2(\mathbf{L3\text{-}3})Cl_2]\cdot H_2O$[b]	solid	15300
	sol'n (CH_3OH)	16500, 14500(sh)
$[Cu_2(\mathbf{L3\text{-}3})SO_4]\cdot 2H_2O$	solid	15600
	sol'n (H_2O)	16500, 14500(sh)
$[Cu_2(\mathbf{L2\text{-}3})Cl_2]\cdot 2H_2O$	solid	17500-15000
	sol'n (CH_3OH)	18000-15000
$[Ni_2(\mathbf{L2\text{-}3})Cl_2]\cdot 2H_2O$	solid	18200
	sol'n (CH_3OH)	18000
	sol'n (pyridine)	18100
$[Ni_2(\mathbf{L2\text{-}2})Cl_2]\cdot 3H_2O$	solid	18300
	sol'n (CH_3OH)	18200
	sol'n (pyridine)	18200
$[Cu_2(\mathbf{L2\text{-}2})Cl_2]\cdot C_2H_5OH.2H_2O$	solid	17400
	sol'n (CH_3OH)	18100

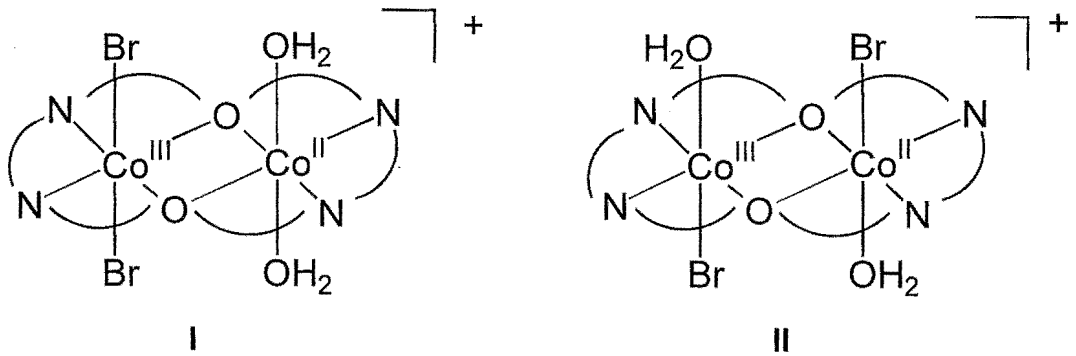
Okawa and Kida prepared complexes of **L2-2**, **L2-3**, and **L3-3**[133] by "stepwise" template synthesis and characterised these by electronic and vibrational spectroscopy. This group suggested[124] that the very broad d-d transition observed for $[Cu_2(\mathbf{L2\text{-}3})\ Cl_2]\cdot 2H_2O$ might indicate two different coordination

geometries for the metal ions. The visible spectra of the $[Ni_2(\mathbf{L2\text{-}2})Cl_2]\cdot 3H_2O$ and $[Ni_2(\mathbf{L2\text{-}3})Cl_2]\cdot 2H_2O$ complexes of **L2-2** and **L2-3** indicated that these complexes were diamagnetic and square planar with this being corroborated by the lack of a significant change in spectra upon going from solid to solution, in either methanol or pyridine. The single d-d transition observed for $[Cu_2(\mathbf{L2\text{-}2})Cl_2]\cdot EtOH\cdot 2H_2O$ indicates square planar geometry. From these results it would seem that, at least with respect to Cu^{2+} and Ni^{2+}, the coordination in this macrocyclic Schiff base system changes from square planar to square pyramidal as the size of the macrocycle is increased. The **L2-2a**Cu_2 complex was assigned square planar coordination geometry from the single d-d transition at 18000 cm^{-1} and the depressed magnetic moment of 0·79 B.M. per Cu (at R.T). This ligand apparently imposes a coordination geometry like the related tetrakis Schiff base **L2-2**.

Since **L3-3** imposed square pyramidal geometry on a range of cations Robson and Hoskins[100] attempted to use the ligand to impose this unusual geometry on Co(III), a metal ion which normally has a very strong preference for octahedral geometry. It was hoped that that this might lead to unusual configurations and/or reactivity at the metal centre. Attempts to generate binuclear Co(III) complexes of **L3-3** by oxidation of the existing chloro complex $[Co^{II}_2(\mathbf{L3\text{-}3})Cl_2]\cdot 2H_2O$[8], using either chlorine or (dichloroiodobenzene), led to a general disruption of the ligand. For this reason a new bromo derivative $[Co^{II}_2(\mathbf{L3\text{-}3})Br_2]\cdot CH_3OH$ was prepared. The crystal structure of this derivative showed it to contain two square pyramidal Co(II) and a methanol of crystallisation which was sometimes weakly bonded. Recrystallisation of this complex from water gave the complex $[Co^{II}_2(\mathbf{L3\text{-}3})Br_2]\cdot H_2O$ in which the methanol was replaced with water. Oxidation of $[Co^{II}_2(\mathbf{L3\text{-}3})Br_2]\cdot CH_3OH$ was undertaken with molecular bromine. If the starting material was mixed with a large excess of molecular bromine at RT a black amorphous precipitate with a high variable bromine content resulted. Heating this precipitate at 60°C under vacuum resulted in a complex identified as $[Co_2(\mathbf{L3\text{-}3})Br_4]\cdot CH_3OH$. This tetrabromo derivative could also be formed by mixing equimolar amounts of $[Co^{II}_2(\mathbf{L3\text{-}3})Br_2]\cdot CH_3OH$ with Br_2 in MeOH at RT and drying the resulting black crystalline precipitate under

vacuum at RT. If the starting material was mixed with equimolar amounts of Br_2 in boiling MeOH another product $[Co^{II}Co^{III}(\mathbf{L3\text{-}3})Br_3]\cdot H_2O$ resulted. The presence of water, not MeOH, in this complex surprised the investigators and was attributed to water being present in the MeOH. C.V and chemical analysis of the tri- and tetrabromo- compounds appeared to support the oxidation state formulations of Co(II)-Co(III) and Co(III)-Co(III) respectively. Both these compounds exhibited Curie-Weiss behaviour in the temperature range 300 - 100K. The observed susceptibilities for $[Co^{II}Co^{III}(\mathbf{L3\text{-}3})Br_3]\cdot H_2O$ were interpreted in terms of one diamagnetic Co(III) per binuclear unit and one paramagnetic Co(II) which require an effective moment of 4·8 B.M. at room temperature. The very strong paramagnetic behaviour of $[Co_2(\mathbf{L3\text{-}3})Br_4]\cdot CH_3OH$ initially led the researchers to believe that they had achieved their aim of a cobalt(III) compound in an unusual electronic configuration. However, as subsequently discussed, this was not the case.

Attempts to grow crystals of these two products from MeOH failed. Eventually crystals were obtained when an equimolar methanolic solution of $[Co^{II}_2(\mathbf{L3\text{-}3})Br_2]\cdot CH_3OH$ and bromine was evaporated at boiling point until a solid just started to separate and the solution allowed to cool slowly. However these crystals, although closely related to $[Co_2(\mathbf{L3\text{-}3})Br_4]\cdot CH_3OH$ and $[Co_2(\mathbf{L3\text{-}3})Br_3]\cdot H_2O$, did not have the same form and turned out to be two isomeric forms of $[Co^{II}Co^{III}(\mathbf{L3\text{-}3})Br_2(H_2O)_2]\cdot Br$. Single crystal X-ray studies of both isomeric forms showed the cations existing in **I** (isomer A) and **II** (isomer B) (Fig. 32). Both consist of discrete $[Co^{II}Co^{III}(\mathbf{L3\text{-}3})Br_2(H_2O)_2]^+$ cations and bromide anions.



I II

Figure 32

Table 2 : Magnetic Properties[100]

Compound	μ_{eff} [a] (B.M.)	Weiss Constant (°K)
$[Co^{II}_2$(**L3-3**)$Br_2]\cdot CH_3OH$	4·68[b] (304)	-55
$[Co^{II}_2$(**L3-3**)$Cl_2]\cdot 2H_2O$	4·61[b] (297)	-62
$[Co^{III}Co^{II}$(**L3-3**)$Br_2]\cdot H_2O$	4·53[b,d] (296)	
$[Co^{III}Co^{II}$(**L3-3**)$Br_3]\cdot H_2O$	4·76[c] (292)	-21
$[Co^{III}Co^{II}$(**L3-3**)$Br_4]\cdot CH_3OH$	4·64[c] (303)	-20
$[Co^{III}Co^{II}$(**L3-3**)$Br_2(CH_3OH)_2]\cdot(Br_3)$	4·46[c] (297)	

[a]Temperature (°K) in parentheses. Susceptibilities were corrected for diamagnetism using the diamagnetic susceptibility of **L3-3** from the measured susceptibilities of $[Zn_2$(**L3-3**)$Cl_2]\cdot 2H_2O$ [8] and Pascal's constants. Measured by Gouy method except for [d]. [b]Moments calculated per Co atom. [c]Moments calculated assuming equal numbers of diamagnetic and paramagnetic Co atoms. [d]Measured at RT only vibrating sample magnometer.

Attempts to grow crystals of the $[Co_2$(**L3-3**)$Br_4]\cdot CH_3OH$ complex from mixtures of $[Co^{II}_2$(**L3-3**)$Br_2]\cdot CH_3OH$ and bromine in MeOH yielded crystals that X-ray studies showed to be $[Co^{II}Co^{III}$(**L3-3**)$Br_2(CH_3OH)_2]\cdot Br_3$ containing a tribromide anion. The crystal structure of $[Co^{II}Co^{III}$(**L3-3**)$Br_2(CH_3OH)_2]\cdot Br_3$ showed it to consist of tribromide anions and two non-equivalent but very similar types of binuclear cation $[Co^{II}Co^{III}$(**L3-3**)$Br_2(CH_3OH)_2]^+$ (Fig.33) and that both of these closely resembled the A isomer of $[Co^{II}Co^{III}$(**L3-3**)$Br_3]\cdot H_2O$. This led to the reformulation of $[Co_2$(**L3-3**)$Br_4]\cdot CH_3OH$ as $\{[Co^{III}Co^{II}$(**L3-3**)$Br_2CH_3OH]^+\}_2\cdot[Br^-(Br_3^-)]$ in which the cation is closely related to the Br_5 (Fig. 33) complex except that the Co(II) has lost one MeOH molecule to become square pyramidal. The electronic spectra of all these complexes were dominated by very intense bands, probably of $n\rightarrow\pi^*$ origin, obliterating any diagnostically useful $d\leftrightarrow d$ bands which may have confirmed the 5-coordinate species proposed for some of these complexes.

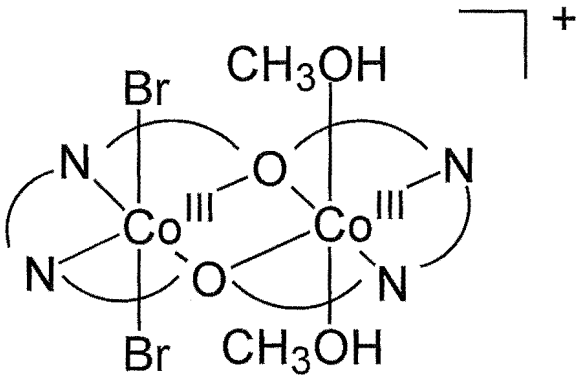


Figure 33

As the structural data indicated that this macrocycle could accommodate two metals within the $N_2O_2N_2$ plane (particularly if one was Co(III)) and additional monodentate ligands could complete the usual pseudo-octahedral ligand fields the researchers were faced with the question as to why the second cobalt atom was so reluctant to become Co(III) even in the presence of excess oxidant. It seemed that a binuclear Co(III)-Co(III) compound did form, but this reverted readily to Co(II)-Co(III). When the original black precipitate formed on the way to the $\{[Co^{III}Co^{II}(\mathbf{L3\text{-}3})Br_2CH_3OH]^+\}_2\cdot[Br^-(Br_3^-)]$ complex was analysed immediately upon its formation, its composition closely corresponded to $[Co_2(\mathbf{L3\text{-}3})Br_8]\cdot 4CH_3OH$. This material was diamagnetic and became paramagnetic as molecular bromine was lost. This initially formed precipitate was assigned the formulation $[Co^{III}_2(\mathbf{L3\text{-}3}^{2-})(Br^-)_2(Br_3^-)_2]$ with two Br_3^- ligands and both metal centres in the preferred (for Co(III)) pseudo-octahedral, low-spin state. The investigators concluded that there was a very powerful driving force for one of the two cobalt(III) centres to become cobalt(II) even though the latter may remain pseudo-octahedral and that, in the solid phase, the Co(III)-Co(III) species was a sufficiently strong oxidant to liberate bromine from the tribromide ion, reversing the process of its formation in solution.

The reasons why a square pyramidal cation geometry was preferred for the divalent metals and why cobalt(III) was so unstable when incorporated, especially when both metal centres were cobalt(III), seemed to be related to variations of some subtle form of strain in the macrocycle. Despite the fact that the dimensions of the cavity for the Co(II) were barely different in all four complexes, the Co(II) in the $[Co_2(\mathbf{L3\text{-}3})Br_2]\cdot CH_3OH$ complex lies 0·30 Å above the N_2O_2 plane whereas the Co(II) in the three different Co(II)-Co(III) complexes is strictly in-plane.

A variable-temperature magnetic susceptibility study of the **L3-3** system was undertaken by Hendrickson and Lambert.[134] It was found that the Cu(II) complex exhibited strong antiferromagnetic exchange (J = -294 cm^{-1}) and that the net antiferromagnetic interaction decreased monotonically across the homobinuclear series Cu(II) (J = -294 cm^{-1}), Ni(II) (J = -27 cm^{-1}), Co(II) (J = -9·3

cm^{-1}), and Fe(II) (J = -4·2 cm^{-1}) with a net ferromagnetic exchange interaction in the Mn(II) complex where J = +0·2 cm^{-1}). It was decided that this decrease in antiferromagnetic exchange was due to several factors. Firstly, according to Anderson's theory,[135,136] superexchange occurs because metal d-orbitals, which contain the unpaired spins, overlap with filled s and p orbitals of the bridging diamagnetic ion. Overlapping of unpaired electron orbitals on the two metals via an overlap with the orbitals of the bridge, mediates an antiferromagnetic interaction. Ferromagnetic interaction pathways were also being introduced across the series leading to a reduced net antiferromagnetic interaction. Unpaired electrons in t_{2g} orbitals, increasing from zero in Ni to three in Mn, introduce ferromagnetic exchange pathways. Secondly, across the series there was a change in the M···O···M angle and this had been shown in a study by Hatfield and Hodgson[137,138] to affect the magnetic interaction. In the system they studied they had shown that for Cu···O···Cu angles greater than ~ 97·6° the interaction was antiferromagnetic while angles less than that led to ferromagnetic interchange. In Cu_2**L3-3** the Cu···O···Cu angle in the X-ray structure was 104·5° and this would be expected to lead to an antiferromagnetic coupling as observed. A further factor in the observed trend across this series is the displacement of the metal ions from the mean plane of the ligand. The two copper(II) ions were located 0·21Å on either side of the ligand plane leading to some reduction in the effectiveness of the antiferromagnetic interaction. The dominant exchange pathway via the copper $d_{x^2-y^2}$ orbitals interacting with the s and p orbitals of the oxide ion, the σ overlap is reduced as the Cu(II) ion moves out of the plane. In going from Cu_2**L3-3** to Ni_2**L3-3** the Ni(II) ion is displaced even more from the ligand plane than Cu(II) further reducing this overlap. In addition, in the Ni(II) complex the introduction of an unpaired electron in the d_{z^2} orbital brings about ferromagnetic exchange pathways. The X-ray structure of the Co(II) complex showed a continuation of this trend. In the Mn(II) complex an even greater metal ion displacement, coupled with large ferromagnetic exchange pathways, led to the observed net ferromagnetic interaction.

Gagné *et. al.*[35] synthesised a series of binuclear complexes **L3-3**$^{2+}M_A^{II}M_B^{II}$, where M_A(II) = Cu(II) and M_B(II) varied across the series Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II), and investigated the redox properties, magnetics and ligand binding of these complexes. The magnetic exchange interchange of this heterobinuclear series of compounds of **L3-3** was of particular interest as the two metal coordination sites were equivalent. They had previously found[127] that the net antiferromagnetic exchange interaction decreased monotonically across a series of homobinuclear complexes, as the metal was changed in the order of Cu(II), Ni(II), Co(II), Fe(II), and Mn(II) and that in the case of Mn(II) a cross-over to a feebly ferromagnetic ground state was observed. A second series of homobinuclear complexes, in which two trans-axial ligands forced each metal ion to lie within the plane of the macrocycle was investigated by these researchers.[108] The magnetic interactions observed for these pseudooctahedrally coordinated metal ions were very similar to those observed for the five-coordinate complexes, in spite of the gross changes in molecular geometry, suggesting that there was one major factor determining the variation of magnetic exchange interaction in the series. This had led to the conclusion that molecular structure was less important than electronic structure (i.e. the number of unpaired electrons and the exchange pathways) in attenuating the exchange coupling parameter. In the heterobinuclear series large changes were also observed in traversing the series in one-electron intervals and again the monotonic trend toward decreasing antiferromagnetic interaction in moving from Cu to Mn was observed.

Other mixed-metal complexes had been prepared and studied by magneto-chemistry but, without exception, each of the binucleating ligands in these studies[139-141] had two inequivalent coordination sites (Fig 34). The same general trend of a net decrease in antiferromagnetic coupling as the metal ion interacting with the N_2O_2/Cu^{II} varies in the order Cu(II), Ni(II), Co(II), and Mn(II) was observed. Gagné's group compared these results to their own and concluded that the observed differences across the series might be explained in terms of structural changes within the complexes e.g. changes in the Cu···O···M angle, as Sinn had suggested.[142]

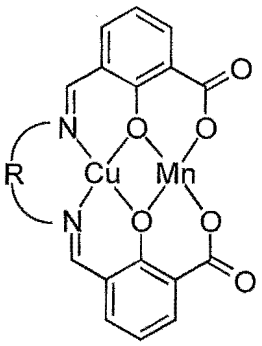


Figure 34

Gagné's heteronuclear complexes had been designed to minimise structural effects accompanying redox changes, to keep coulombic interactions constant and cancellable, and to permit superexchange effects to be measured separately. It was expected that electrochemical measurements would then enable a determination of electronic delocalisation energies in mixed-valent species. For the **L3-3**$Cu^{II}M_B^{II}$, in which the Cu(II)/Cu(I) reduction potentials were measured as a function of the remote metal, this worked very well as, within experimental error, the Cu(II)/Cu(I) reduction potentials were independent of the remote metal M_B unless M_B was copper(II) (Table 3).[35] In comparison to the heterobinuclear species, it is easier to add an electron to the Cu(II)-Cu(II) species by an average of 143 mV or 3·3 kcal mol^{-1} and this difference is ascribed to the fact that only the **L3-3**$^{+}Cu^{I}Cu^{II}$ can exist, to any extent as a resonance-stabilised, delocalised ion. This electronic delocalisation energy is the major contribution to the 3·3 kcal mol^{-1}.

Table 3 : Reduction Potentials the Cu^{II}/Cu^{I} Couple as a Function of the Remote Metal M_B^{II}

	cyclic voltammetry[b]		differential pulse[c] polarography		sampled DC[d] polarography		Coulometric	
Starting Cpd	E_f, V	$VE_{p_a} - E_{p_c}$, V	E_p, V	fwhm,	$VE_{1/2}$, V	slope, V	*n* value	$E_f(\sigma)$[b], V
$Cu^{II}Mn^{II}L^{2+}$	-1·080	0·120	-1·070	0·095	-1·052	0·062		-1·070(10)
$Cu^{II}Fe^{II}L^{2+}$	-1·058	0·060	-1·050	0·095	-1·068	0·062	0·98	-1·063(12)
$Cu^{II}Co^{II}L^{2+}$	-1·070	0·070	-1·060	0·120	-1·067	0·061		-1·066(6)
$Cu^{II}Ni^{II}L^{2+}$	-1·090	0·080	-1·092	0·100	-1·055	0·060		-1·074(29)
$Cu^{II}Cu^{II}L^{2+}$	-0·930	0·070	-0·932	0·092	-0·917	0·058	1·0	-0·925(8)
$Cu^{II}Zn^{II}L^{2+}$	-1·060	0·070	-1·060	0·100	-1·076	0·058	0·95	-1·067(15)

[a] All measurements taken in DMF solvent with 0·1M tetrabutyl ammonium perchlorate as the supporting electrolyte. Data in V vs Fc/Fc^{+}. Formal reduction potentials, $E_f(\sigma)$, are weighted average values of the measured potentials. [b] Scan rate - 0·5 V/s. Working electrode = Pt button. [c] Peak potentials measured with Pt button electrode. Scan rates = 1-10 mV/s. [d] Half wave potentials measured by using dropping Hg electrode at a scan rate of mV/s. Drop time was 5 s. [e] Coulometric *n* values measured by electrolysis using a Pt gauze electrode. [f] Average formal potentials with 1 esd.

This group found[143,109] that the **L3-3**Cu(II)Cu(I), which they generated by cyclic voltammetry, exhibited unusual temperature-dependent EPR behaviour. Solution EPR spectra showed the seven lines consistent with the odd electron interacting with both Cu centres. This was in marked contrast to Addison's findings[131] for the analogous 2,6-diacetyl-4-methylphenol complex which exhibited the four-line EPR spectrum indicating the charge was localised on one Cu only at room temperature in CH_3CN. Robin and Day[144] have classified complexes in which the electron is localised on one metal as being Class I whereas Class II complexes are those in which delocalisation does take place but the two types of site are still distinguishable and so the electron does not spend equal times on them.* In Class II complexes the electron becomes localised at low temperatures. However, when the **L3-3** complex was frozen (77 K) this four-line anisotropic spectrum was also seen. Similarly if CO was added to the complex the four-line spectrum was observed. It may have been that at low temperature axial ligation of ClO_4^- or solvent (CH_3CN or CH_2Cl_2) had led to an asymmetric complex comparable to the carbonyl adduct, or that macrocyclic ligand conformational changes which accompany electron exchange (possibly distorted tetrahedral for Cu(I) to distorted square planar for Cu(II)) become more difficult in frozen solutions resulting in a "locked-in" configuration on the EPR time scale. From the temperature dependent EPR studies a rate of $1{\cdot}7 \times 10^{10}$ s^{-1} was estimated for the thermal intramolecular transfer.[109]

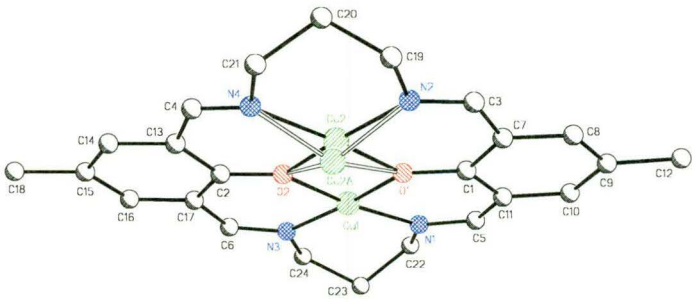


Figure 35 : The cationic core of the Cu(II)Cu(I)L3-3 complex showing the disordered position of the monovalent copper ion.

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* Robin and Day go on to say that it is "not easy to draw a precise demarcation between Classes I and II but, in the vast majority of cases, Class II systems have at least one ligand which bridges the two ions of differing valency, whereas in Class I systems the metal ions are either removed from one another by two or more ligands which are relatively non-interacting, or have very different coordinations."

In a subsequent X-ray structure determination of the Cu(II)Cu(I) complex[145] (Fig. 35) it was shown that there were distinct copper coordination sites in the solid state. The divalent copper (Cu1) exhibited typical square planar geometry but the monovalent copper ions (Cu2 and Cu2a) were disordered about two sites 0·51 Å apart with populations of 35% and 65% respectively. The coordination of the more populated site was only approximately square pyramidal (or distorted tetrahedral) whereas the other copper atom was square pyramidal. The geometry of the distorted site is closer to that (tetrahedral) preferred by Cu(I).

Addison[131] reported an increase of ~0·1V in the reduction potential of the dicopper complexes in passing from **L3-3a** to **L4-4a**. This was attributed to an increased stabilisation of the tetrahedral stereochemistry favoured by the Cu(I) complex **L4-4a** probably as a result of the added flexibility of this ring. The ESR spectrum of **L3-3a** showed that the unpaired spin resided on one copper atom.

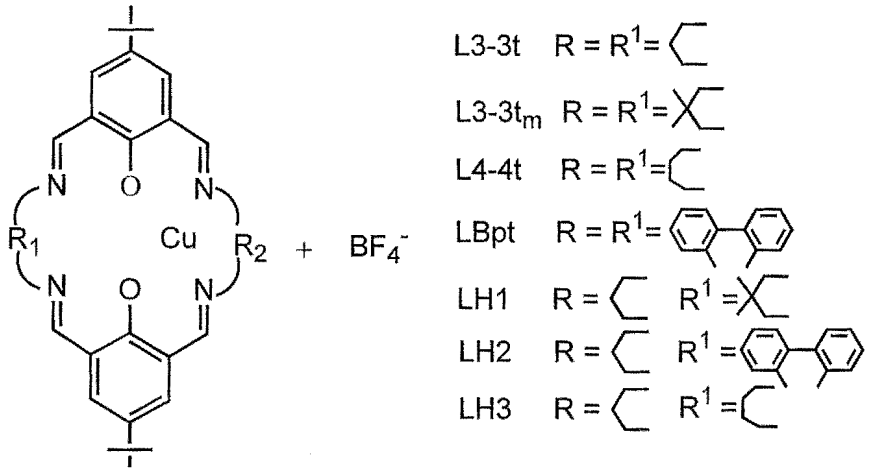


Figure 36

To study the factors affecting intramolecular electron transfer Hendrickson *et. al.*[52] prepared a series of seven mixed-valence binuclear copper(II)-copper(I) complexes of **L3-3t, L3-3t$_m$, L4-4t**. These are similar to those of Gagné,[109,143, 145] but with the methyl groups on the phenolic unit replaced by *tert*-butyl substituents. Additional variations were introduced into the macrocycles by modifying the lateral chains **LBpt,** and incorporating two different chains into some of the ligands (**LH1, LH2, LH3** Fig. 36). These complexes were reduced chemically, using sodium dithionite, to produce the mixed valence species. It

was hoped that this selection of diamines would produce considerable variation in the N_2O_2 copper coordination geometries. In particular the 2,2'-biphenyl linkage, which had a non-zero dihedral angle between the two phenyl moieties, should show a geometry intermediate between square planar and tetrahedral. It was expected and shown that the electrochemical data should reflect these differences.

At RT the solution EPR spectra indicated delocalisation of the single electron for the first four complexes but for the other three the electron was localised at one centre whereas Gagné's complexes all showed the seven-line pattern typical of delocalisation. Electrochemical studies showed that the interaction of the electronic manifolds of the two copper ions in a given $Cu^{II}Cu^{II}$, $Cu^{II}Cu^{I}$, or $Cu^{I}Cu^{I}$, complex does not change much as the copper coordination is changed in the series.

Nag *et. al.*[122,128] extended Gagné's work by studying the cyclic voltammetry of the series of dicopper(II) complexes of **L3-3, L3-3a, L3-3b, L3-3c, L3-3d, L3-3e, L3-3f, L3-3g, L3-3h** with the aim of establishing the varying degrees of stabilisation of the mixed-valence complexes obtained by making subtle and cumulative variations in the macrocyclic ligand structure. They also wished to know whether the potentials for the addition of the first electron would be dependent on the extent of the magnetic interactions in the dicopper(II) complexes. Gagné had proposed that the first electron is transferred at the triplet state and had shown that for a system having $J \sim -300$ cm^{-1} that the observed potential differed by only 6 mV from the potential calculated for the $J = 0$ hypothetical system. This predicted that for related compounds the potentials for the first reduction step would be virtually independent of the extent of magnetic interaction. The room temperature magnetic moments of Nag's complexes ranged from 0·4 (**L3-3b**) to 0·8 B.M.(**L3-3c**) and at the time of writing the antiferromagnetic coupling constants (J) had not been determined. Calculations, however showed that the J values of the five complexes should vary significantly ($J \geq -290$ cm^{-1}) and therefore they should provide an opportunity to test the mechanism of electron transfer. It was noted that the

potentials of the first couple remained invariant throughout the series clearly supporting Gagné's hypothesis.

The ligand binding properties of these complexes were also investigated[35] and the results (Table 4) show that for weakly binding bases such as ethene or 4-ethylpyridine any significant variations in binding parameters are lost in experimental noise, but the chemical binding constants for tris(*o*-methoxy-phenyl)phosphine and for carbon monoxide are large and differences in these series were significant. Since the electrochemical data indicated that the heterometal ion M_B^{II} had little effect on the electron density at the copper site, the results were surprising. It was clear that the chemical binding of axial bases to Cu(I) was not independent of the heterometal as the redox potentials implied. It had also been expected that the axial ligands would bind more poorly to the dinuclear copper species relative to the others, since this would likely result in some loss of delocalisation by removing the equivalence of the metals. This also was not observed. It was obvious that the chemical manifestations of metal-metal interactions were not a simple reflection of their redox properties but were a complicated function of several undetermined factors.

Table 4. Equilibrium Constants, K_L", for the binding of Axial Base[a] .

Complex	$10^{-4}K_{CO}$, M^{-1}	K_{CH2CH2}, atm^{-1}	K_{PR3}, M^{-1}	K_{etpy}, M^{-1}
$Cu^{I}Mn^{II}L^{+}$	0·9(3)	0·3(3)	0	22·5(7)
$Cu^{I}Fe^{II}L^{+}$	1·5(4)	0·9(4)	0	28(6)
$Cu^{I}Co^{II}L^{+}$	0·9(5)	0·3(3)	0	10·2(6)
$Cu^{I}Ni^{II}L^{+}$	1·5(4)	0·4(3)	$4·1(4)x10^{2}$	30(4)
$Cu^{I}Cu^{II}L^{+}$	3·1(3)	1·5(3)	$1·2(2)x10^{3}$	38(14)
$Cu^{I}Zn^{II}L^{+}$	1·1(4)	1·6(3)	0	9·7(17)

[a] Measurements were taken as a function of the remote metal ion M_B(II). Substrates (L") studied include carbon monoxide (CO), ethylene (CH_2CH_2), tris(*o*-methoxyphenyl) phosphine (PR_3), and 4-ethylpyridine (etpy). Binding constants were determined by an electrochemical method. Standard deviations appear in parentheses. In all cases, *N,N*-dimethylformamide containing 0.1 M tetrabutylammonium perchlorate was the solvent.

The next development with **L3-3** was to investigate the gradual reduction of the azomethine linkages. Reactivity studies of this system had the potential to be hampered by undesirable reactions at the CH=N centres e.g. hydrolytic disruption of the macrocycle, whereas the poly-amino ligands in which the

CH=N links had been replaced by CH_2-NH promised to be more robust enabling reactivity studies to be undertaken under harsher conditions. Nag noted in the course of his studies of the tetraamino diphenol macrocycles that, owing to the greater flexibility and stronger σ-donor capacity of secondary amines, the stereochemistry and redox and magnetic properties of these complexes differed significantly from their Schiff base analogues. Nag was also quick to recognise the advantage of using the preformed reduced macrocycle to undertake these studies and used Mg^{2+} ions to prepare these.[66]

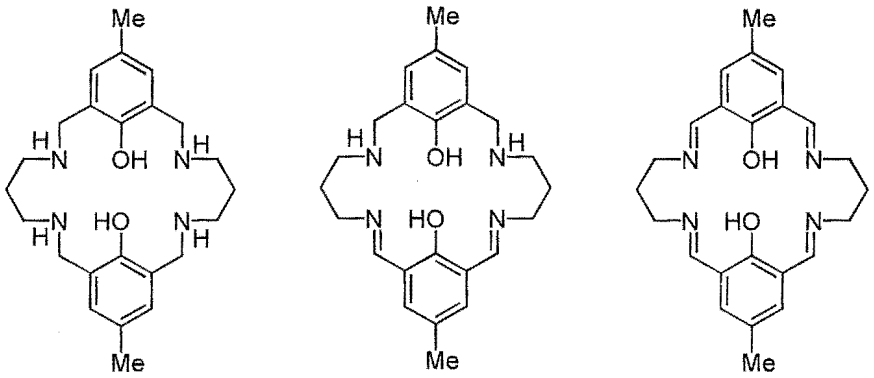


Fig. 37 : The fully reduced (L3-3_R), partially reduced (L3-3_{PR}), and diimine forms of L3-3

Nag investigated the partially reduced **L3-3_{PR}**[114,128] and then the fully reduced **L3-3_R** (Fig 37).[64] These reductions were effected electrochemically. His system was the first case where it was claimed a magnetically coupled macrocyclic binuclear copper(II) system can involve two successive one-electron oxidation steps to produce Cu(II)-Cu(III) and Cu(III)-Cu(III) species as well as successive one-electron reduction steps to produce mixed-valence Cu(II) - Cu(I) species and binuclear Cu(I) species. Nag also showed that in the $Cu^{I}Cu^{II}$ **L3-3_R** complex the single electron was interacting with just one copper centre (I = 3/2). Nag and Das[6] later showed that the Ni(II) complex of **L3-3_R** also underwent these four one-electron transfers to generate dinickel species with oxidation states varying between +1 and +3. **L3-3_R** exhibited very strong antiferromagnetic coupling between the two copper(II) centres. It was noted that as the degree of reduction increased the intensity of the charge-transfer transition in the UV region decreased while that of the visible absorption increased.

Okawa's team[147] extended Nag's investigation to the dicopper complexes of the series **L2-3$_R$**, **L2-4$_R$**, **L2-5$_R$**, **L3-3$_R$**, and **L3-4$_R$** which they prepared by the reduction, using $NaBH_4$, of the unsaturated $(Lm,n)^{2-}$ analogues of their Cu_2Pb complexes.[141] Their aim was the study of the differences in the physico-chemical properties of the saturated and unsaturated systems, with particular interest in the mixed valence $Cu^{I}Cu^{II}$ series whose stability and electronic properties they reported. It appeared, from the cyclic voltammetry of these compounds, that the saturated macrocycles stabilise the higher oxidation state Cu(III) but destabilise the lower oxidation state Cu(I) relative to the unsaturated macrocycle. The unsaturated macrocycle can accept electrons from copper(I) through the antibonding orbitals of the C=N linkages whereas the saturated macrocycles act solely as electron donors. The mixed $Cu^{I}Cu^{II}$ complexes were generated electrochemically and subjected to ESR and visible spectral studies. The ESR of the Cu_2**L2-4$_R$** complex showed it to be "spin-trapped" and belonging to Class I of Robin and Day's classification.[144] The same spin localisation on one copper in the $Cu^{I}Cu^{II}$ state had been reported for complexes of **L2-3$_R$, L2-4$_R$, L2-5$_R$, L3-3$_R$, L3-4$_R$** by Nag *et.al.*[64]

The Cu_2Pb complex just referred to in Okawa's study of saturated and unsaturated systems, was one of a series of hetero Cu_2Pb and Ni_2Pb complexes he had made while attempting to find a new route to the hetero-bimetallic complexes of **L2-2, L2-3, L2-4, L2-5, and L3-3.**[148] The direct template method had been found to be only suitable for the macrocycles in which the alkane chains were the same length ($m = n$) and the stepwise template reaction had given very poor yields for the synthesis of macrocycles with longer alkane chains [$m(n) > 3$]. His new route involved the reaction of N,N'-Ethylenebis(3-formyl-methylsalicylideniminato)]-nickel(II) and -copper(II) or N,N'-propane-1,3,diylbis(3-formyl-methylsalicylideniminato)]-nickel(II) and -copper(II)[133,124] with a lead salt and the appropriate diamine. However, this reaction did not yield the expected binuclear hetero- products but rather trinuclear dimeric complexes in which the macrocycle incorporated a nickel or

copper ion into the N_2O_2 donor site and was bridged by a lead ion. Figure 38 illustrates the $[PbCu_2(\mathbf{L3\text{-}3})(ClO_4)_2]\cdot DMF$ complex.

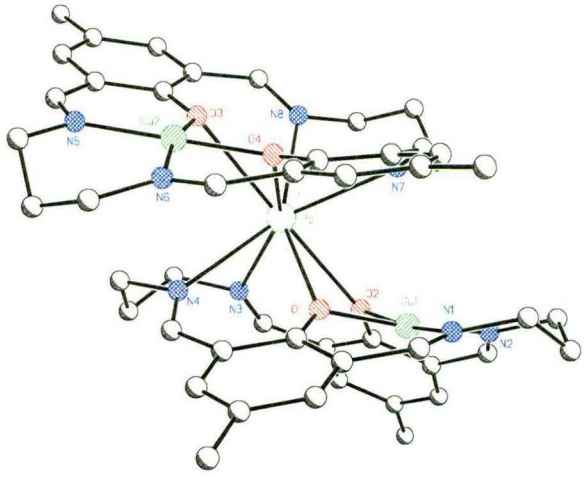


Figure 38

The magnetic behaviour of the reduced ligand system was investigated by Nag *et. al.*[152] Antiferromagnetic behaviour had been observed for the binuclear nickel(II) complexes of **L3-3**[108,134] and its 2-hydroxy derivative **LV3**[48]. A linear relationship[138] had been found for the value of *J* and the Cu···O···Cu bridge angle in the planar dihydroxo-bridged copper(II) complexes but a similar magnetostructural correlation had not been found in nickel(II) complexes of **L3-3** because a large number of structural parameters seemed to affect the superexchange mechanism for these systems. Nag decided to see if such a correlation could be established for nickel complexes of the reduced ligand system. It was felt that by varying the axial ligands on a series of binuclear nickel(II) complexes of $\mathbf{L3\text{-}3_R}$ they might influence exchange interactions, especially if this produced stereochemical changes. Across the series :

1 : $[Ni_2\mathbf{L3\text{-}3_R}(H_2O)_4]\cdot(ClO_4)_2\cdot 4NH_2CONH_2$

2 : $[Ni_2\mathbf{L3\text{-}3_R}(NCS)_2(H_2O)_2]\cdot 2Me_2NHCO$

3 : $[Ni_2\mathbf{L3\text{-}3_R}\,(MeOH)_2(ClO_4)_2]\cdot 2NHEt_3ClO_4$

4 : $[Ni_2\mathbf{L3\text{-}3_R}(im)_2]\cdot(ClO_4)_2$

5 : $[Ni_2\mathbf{L3\text{-}3_R}(py)_4]\cdot(ClO_4)_2$

6 : $[Ni_2\mathbf{L3\text{-}3_R}(\mu\text{-}O_2CCH_2NH_3)(H_2O)_4]\cdot(ClO_4)_2\cdot 2H_2O$

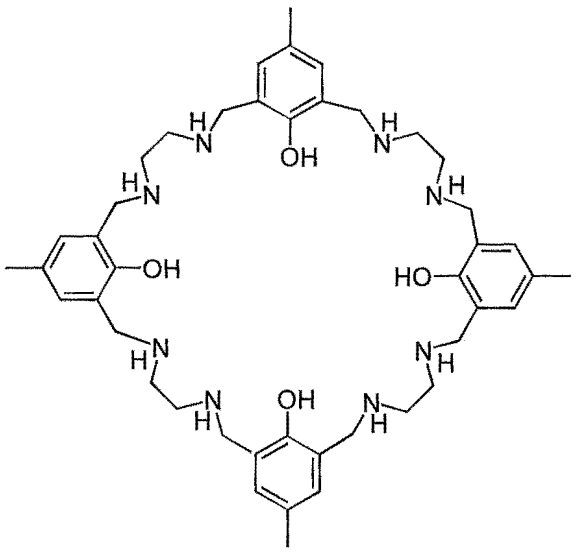
they found that the antiferro-magnetic exchange interaction appeared to increase with the increase of the bridge angle involved in the superexchange

pathway where the bridge angle was systematically increased in passing from octahedral to elongated tetragonal to square pyramidal geometries. Only complex **6** whose structure was different from the others did not follow this trend. Complex **6** contained an additional superexchange pathway, perpendicular to the Ni_2O_2 pathway, involving the carboxylate bridge of the glycine zwitterion. Certainly the study showed that, in comparison to the unreduced ligand system, there was a dependence of the exchange parameter on the stereochemistry of the metal centres and that tuning of spin exchanges in complexes of this sort ought to be possible with variations in the structures.

In 1994 Nag[149] extended his studies to use the preformed ligand to investigate the cobalt(II), iron(II) and manganese(II) complexes of **L3-3$_R$**. Although the manganese(II) and cobalt(II) complexes - $[M_2(\mathbf{L3\text{-}3_R})(CH_3OH)_2X_2]\cdot 6H_20$ (X = Cl or Br) - could be readily obtained by reacting the metal salts, ligand, and triethylamine in the ratio 2:1:1, Mossbauer spectra showed that the iron(II) complexes had some Fe^{3+} impurity if prepared this way. This was overcome by using imidazole as an auxiliary ligand with $Fe(ClO_4)_2$ to produce the red crystalline product $[Fe_2(\mathbf{L3\text{-}3_R})(im)_2(CH_3OH)_2]\cdot(ClO_4)_2$. The dicobalt and dimanganese complexes were oxidised with bromine to produce the mixed-valence $Co^{III}Co^{II}$ and $Mn^{III}Mn^{II}$ complexes but from the analogous reaction with diiron no definite product could be isolated. Six-coordinate geometry was proposed for these complexes on the basis of their chemical composition, molar conductivity and room temperature magnetic moments.

UV-vis spectra showed features consistent with this geometry but more typical of distorted tetrahedral geometry. As previously mentioned, in both the imine containing **L3-3** dicobalt(II)[132] and dimanganese(II)[150] complexes, where crystal structures have been determined, the coordination environment of the metal centres is square pyramidal. The stereochemical differences, shown here, between the complexes of **L3-3** and **L3-3$_R$** also occur in the dicopper(II) and dinickel(II) series. Because of the rigidity of the **L3-3** macrocycle the metal ions are displaced from the ligand plane in opposite directions and acquire the square pyramidal geometry, whereas in the case of the more flexible **L3-3$_R$** the

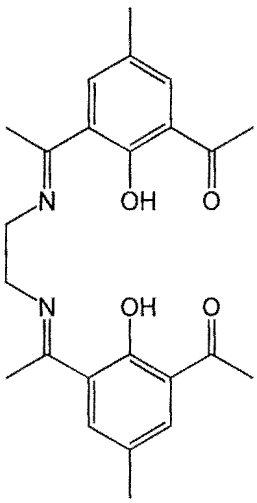
metals are accommodated in the ligand plane and achieve distorted octahedral geometry. The results from magnetic studies of these complexes showed that for the diiron case there were antiferromagnetic exchange interactions lying within the range of those found for a series of diiron complexes[108] of the **L3-3** ligand indicating that the same mechanism of spin exchange involving the phenoxide bridge is operative in both types of complexes. In contrast, the *J* value, -6·1 cm^{-1}, for the $[Mn_2(\mathbf{L3\text{-}3}_R)Br_2]$ complex , differs significantly from the weakly ferromagnetic $[Mn_2(\mathbf{L3\text{-}3})Cl_2]$ complex for which J = 0·2 cm^{-1}. The manganese ions in these two complexes differ in their stereochemistry being six coordinate in the first case and square pyramidal in the second and the most important effect of this stereochemical change will be on the phenoxide bridge angle. The magnitude of exchange interaction is most likely affected by variation of the bridge angle and, as already reported here,[151,152] a wide range of *J* has been shown to occur for a series of dinickel(II) compounds of **L3-3** where the bridge angle was systematically increased in passing from octahedral to elongated tetragonal to square pyramidal geometries. But the difference in the two manganese(II) complexes may lie in the fact that one is a bromo and the other is a chloro compound as this group[153] had already shown a difference in the antiferromagnetic exchange coupling in the series $[Cu_2(\mathbf{L3\text{-}3})X_2]$ (X = Cl, Br, or I)



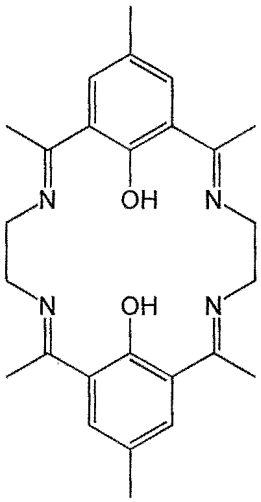
L2-2(4)$_R$

Figure 39

More recently, as part of his investigations into the use of preformed reduced ligands in generating polynuclear complexes, Nag has synthesised a [4 +4] complex from the same starting materials as **L2-2.**[115] Reaction of 2,6-diformyl-4-methylphenol, 1,2-diaminoethane, $Mg(CH_3COO)_2 \cdot 4H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ (4:4:2:2) resulted in the magnesium complex of **L2-2(4)** which was subsequently reduced with $NaBH_4$ in methanol. Ligand $\mathbf{L2\text{-}2(4)_R}$ is shown in Figure 39. In the tetranuclear Ni(II) complex $[Ni_4(\mathbf{L2\text{-}2(4)_R})(\mu_3\text{-}OH)(\mu\text{-}H_2O)_2(ClO_4)] \cdot (ClO_4)_2 \cdot 2CH_3COCH_3 \cdot H_2O$ the four noncoplanar nickel atoms were each in a distorted octahedral environment and the cationic core completely lacked symmetry. Each metal was coordinated to two amine nitrogens and two bridging phenoxide residues. Three of the metals were anchored by the tricoordinated hydroxyl oxygen, each pair of metals was bridged by water molecules and one nickel was bonded to a perchlorate. The complex is notable for the number of hydrogen bonds it contains there being ten intramolecular bonds involving NH, phenoxide, and aqua bridges and six intermolecular bonds involving ClO_4^-, NH, acetone, and water.



L2-2o



L2-2a

Figure 40

Fenton *et.al.*[130] synthesised a series of variations of the **L2-2** ligand as a part of a programme aimed at introducing endogenous bridges into the lateral units. In attempts to produce mononuclear metal complexes of **L2-2o** (Fig. 40) from the condensation of two equivalents of 2,6-diacetyl-4-methylphenol with one of 1,2-

diaminoethane they found (by IR and analytical techniques) that if lead(II) and zinc(II) salts were used, the homobinuclear complexes $[Pb_2(\mathbf{L2\text{-}2a})(NCS)_2]$ and $[Zn_2(\mathbf{L2\text{-}2a})(CH_3CO_2)_2]$ were obtained. These complexes could also be prepared by the usual template method. The binuclear lead(II) complex was unexpected, as the lead ion size (1·06 Å) falls outside the cavity size-cation size matching criterion frequently used in selectivity studies.[154] It was proposed that the steric factors would allow one lead(II) to lie above the plane of the macrocycle with the second lead(II) lying below this plane as had been observed in the crystal structure of the analogous $[Cu_2\mathbf{L2\text{-}2a}(H_2O)_2]\cdot(BF_4)_2$ complex of this ligand[155] where the two copper (II) atoms (0·96 Å) lie on either side of the macrocyclic plane with a displacement from it of 0·18 Å. This displacement of the lead ions is seen in the binuclear lead complex of **LV3** (Fig. 43a, Section 1 : 3 : 1). Crystals suitable for X-ray analysis were unobtainable for Fenton's lead complex but a single imine stretch in the IR indicated that it was symmetrical. When lead(II) perchlorate was used as a templating agent with 2,6-diacetyl-4-methylphenol and 1,3-diaminopropane, a mononuclear complex was formed in which the phenol -OH was not deprotonated.

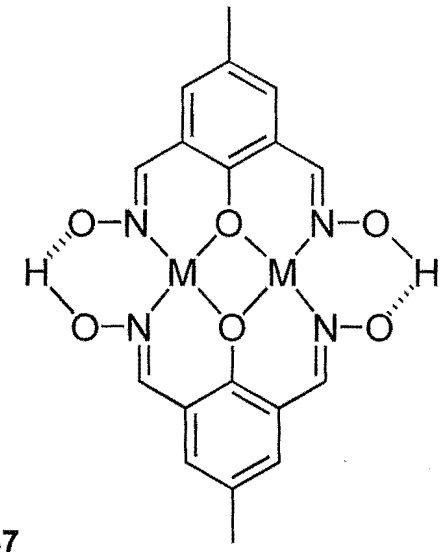


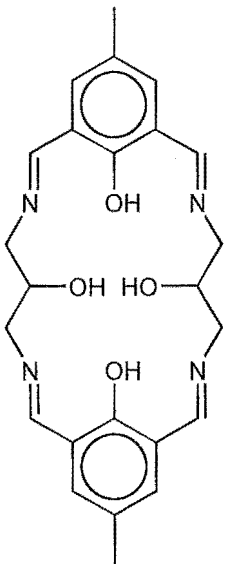
Figure 37

An interesting variation of these macrocycles, which will not be discussed in detail here, is one which the macrocyclic ring is completed by one or more O·····H·····O (Fig. 41). These "hydrogen-bridged" macrocycles were formed by either the mononuclear precursor being reacted with the appropriate hydroxyl-

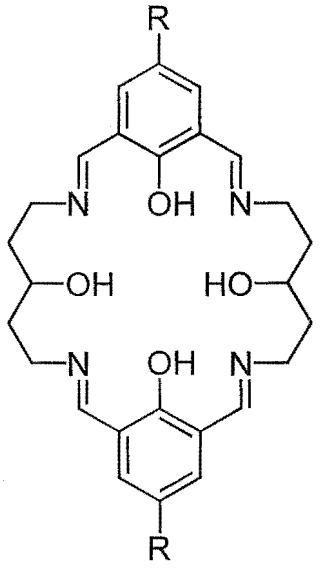
amine and metal salt or by direct reaction of the dialdehyde, hydroxylamine and metal salt.[156] The dinickel(II) complex, which had one side closed with ethylene diamine and the other side hydrogen bridged,[156] was found to have the novel situation in which one Ni(II) ion was diamagnetic and the other was paramagnetic. The complex visible spectrum was interpreted in terms of tetragonal pyramidal geometry around a high spin nickel ion, with DMF as the fifth ligand. The magnetic studies suggested that only one of the nickel ions was high spin. The low spin Ni(II) was expected to have square planar geometry. No apical coordination of DMF is observed in other Ni^{2+} complexes of **L2-2** and so it was proposed that the high spin pyramidal nickel occupied the side of the complex involving the hydrogen bridge.

1·3 : Lateral Chains Incorporating Alcohol Functions

Modification of the Robson macrocycle to incorporate alcohol functions on the lateral chains led to potentially octadentate macrocyclic ligands. McKee *et. al.* first reported the Schiff base condensation of 2,6-diformyl-4-methylphenol with 1,3-diaminopropan-2-ol or 1,5-diaminopentanol to form the H_4**LV3** and **H_4LV5** ligand systems (Fig. 42). Fenton has used 1,3-diaminopropan-2-ol with 2,6-diacetyl-4-methylphenol in a similar ligand system[130]



H_4LV3



H_4LV5

Figure 42

1·3·1 : 1,3-Diaminopropan-2-ol

Using template condensation of 2,6-diformyl-4-methylphenol with 1,3-diamino-propan-2-ol in the presence of $Ba^{2+}$and Pb^{2+} M^{c}Kee's group synthesised mononuclear lead and barium complexes and a binuclear lead complex of the **LV3** ligand.[42] With H^{+} the diaquo complex of the partially protonated macrocycle was formed. The mononuclear lead and barium complexes were shown to have distinctly different coordination attributable to the size of the ions concerned. The reaction of 2,6-diformyl-4-methylphenol and 1,3-diamino-propan-2-ol with lead(II) perchlorate in methanol initially yielded the binuclear complex $[Pb_2(H_2\mathbf{LV3})][ClO_4]_2$, (Fig. 43a) but after standing for several days the mononuclear $[Pb(H_4\mathbf{LV3})][ClO_4]_2$complex (Fig. 43b) and a salt of the protonated macrocycle $[(H_6\mathbf{LV3})(H_2O)][ClO_4]_2$ (Fig. 43c) were obtained. The crystal structure of each of these was determined. The use of $Pb(NCS)_2$ as the templating metal salt produced only a mononuclear product under all conditions tried, as did the use of Ba^{2+}. The macrocyclic ring was apparently too small to accommodate two barium(II) ions.

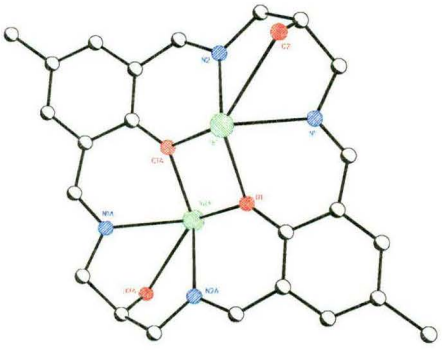


Figure 43a

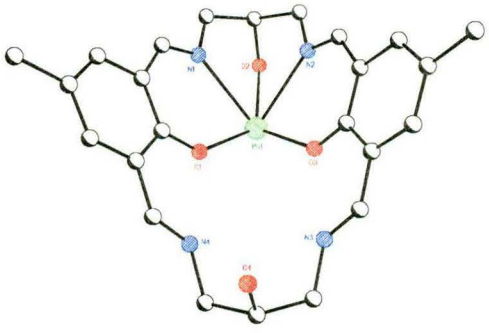


Figure 43b

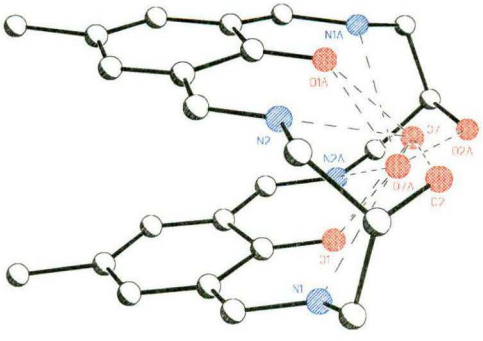


Figure 43c

The protonated macrocycle was also prepared by reaction of 2,6-diformyl-4-methylphenol and 1,3-diaminopropan-2-ol with perchloric acid. This salt of the ligand is folded in a such a way that the two π regions are almost parallel (the phenol rings are inclined at 7° to each other) and are separated by approximately 3·5 Å (Fig. 43c). This configuration is also seen in the barium complex of **LV3a** reported by Fenton.[130] This π interaction probably accounts for the relative stability of the protonated macrocycle and the barium compounds. The similarly folded H_4**L3-3** has been discussed in 1·1.

The structure of the binuclear lead complex was similar to that of transition metal complexes of related ligands[34,109,157] and its tendency to lose the Pb^{2+} is explained by the larger radius of Pb^{2+} relative to the first row transition metals. Pure samples of the binuclear metallated products remained stable even after refluxing for 48 h in methanol so it seemed that the loss of the metal ion from these required the presence of acid in the solution to allow the protonation step to occur. In the centrosymmetric cation of $[Pb_2(H_2$**LV3**$)]^{2+}$ the macrocyclic ring is approximately planar with the lead atoms 1·32 Å out of the mean plane of the nitrogen and phenoxy donors. The metals are five coordinate and each is bonded by two bridging phenoxy groups, two imine nitrogen atoms and one of the lateral alcohol groups though the length of this Pb-O bond, at 2·77(1) Å, suggests that this is rather a weak interaction. In binuclear complexes of this ligand with smaller metal ions it was shown that the alkoxy oxygens were not involved in bonding to the metals but rather turned outwards from the macrocyclic cavity. This out-of-plane displacement of the lead ions is explained by a mismatch of the size of the metal ions and the cavity size and similar displacements have been observed in binuclear transition metal complexes of related ligands.[34,109,157] In this configuration the macrocycle cannot fold to provide a more stable coordination about one lead atom without forcing the expulsion of the second. The mononuclear lead complexes have distinctly different structures (Fig. 43b) to those seen for the barium complexes of **LV3** and related ligands[130] and to the binuclear lead complexes. The ligand is folded with the phenol groups inclined at 100° to each other. It would seem that

the driving force in forming the mononuclear complex would be the increased stability of the metal-ligand bonding.

A similarly folded complex was seen when 1,3-diaminopropan-2-ol was used, by Fenton, in a [2 + 2] condensation with 2,6-diacetyl-4-methylphenol. This reaction in the presence of Ba^{2+}, Sr^{2+} and Pb^{2+} gave both mononuclear and homobinuclear complexes of **LV3a**.[130] The crystal structure of the mononuclear [Ba(**LV3a**)]·$(ClO_4)_2$ complex (Figs. 44a & b) revealed the ligand to be folded in such a way that the two aromatic rings were stacked almost parallel (being situated on planes having a dihedral angle of 178° between them) to each other with the Ba^{2+} sitting "above" the structure with the anions on the opposite side of the metal ion to the ligand (Fig. 44b).

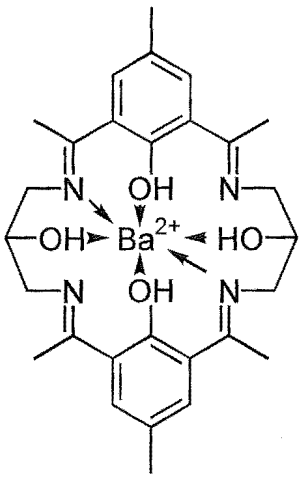


Figure 44a

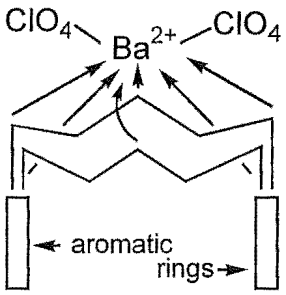


Figure 44b

The barium ion is bound to two diagonally opposite N atoms, both phenolic oxygens, the two alkoxy oxygens and two oxygen atoms from the unidentate perchlorate anions. There is an intramolecular hydrogen bond between the phenolic oxygen and the uncoordinated imino-nitrogen atom. The C-N bond for the bound imine group was found to be longer than for the unbound imine (1·29 Å v 1·27 Å) presumably arising from loss of electron density toward the Ba^{2+} (Fig. 45). It was speculated that the structure of the lead complex would be similar to this; in view of the M^{c}Kee structure(Fig.43b) this would seem likely. From this study, where binuclear complexes were obtained for Sr^{2+} (1·13 Å) and Pb^{2+} (1·06 Å) but only a mononuclear complex with Ba^{2+}, it was concluded

the critical ion radius below which binuclear products result with this ligand **LV3a** is ~ 1·2 Å.

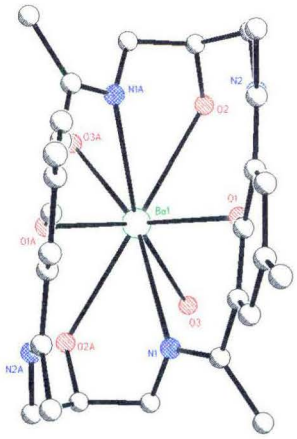


Figure 45

The binuclear copper(II) complex $[Cu_2$**LV3a**$(ClO_4)_2]$ was prepared and the magnetic moment compared to the corresponding $[Cu_2($**L3-3**$)(ClO_4)_2]$ complex.[122] The latter had the reduced value of 0·66 B.M. per Cu atom due to antiferromagnetic coupling mediated by the bridging phenolic groups. The **LV3a** complex was found to have a magnetic moment of 1·20 B.M. and the higher value is thought to arise from either steric changes brought about by the presence of the lateral hydroxy groups or by interaction of these groups either intra- or inter-molecularly with the copper(II) thus altering the mediation by the phenolic units.

M^{c}Kee extended her studies of the **LV3** ligand to a series of binuclear Mn(II) and Ni(II) complexes[48] of the type $[Mn_2(H_2$**LV3**$)X_2]$ where X = Cl^-, Br^-, NO_3^-, NCS^-, CH_3COO^-, N_3^-, and $[Ni_2(H_2$**LV3**$)X_2Y_2]$ where X = Cl^-, Br^-, NO_3^-, and Y = H_2O along with $[Ni_2(H_2$**LV3**$)(NCS_2)(CH_2CH_3OH)]$ and $[Ni_2(H_2$**LV3**$)(CH_3COO)_2]\cdot 2H_2O$ were prepared and characterised by analytical, spectroscopic, magnetic susceptibility measurements, and electrochemical techniques. Single crystal X-ray structures of $[Ni_2(H_2$**LV3**$)(H_2O)_2Cl_2]\cdot 2H_2O$ and $[Mn_2(H_2$**LV3**$)(CH_3COO)_2]$ $\cdot 2CH_3OH$ were determined. In this series the complexes were all binuclear (even when a metal : ligand ratio of 4 : 1 was used). Structurally they are essentially similar to the **L3-3** complexes with the two metal ions bridged by the deprotonated phenolate donors of the macrocycle and the alcohol groups retaining their protons and not coordinated to the metal ions. This contrasts

with their behaviour in the Pb(II) complex and the difference may be attributable to the different nature of the lead ions and the mismatch between the size of the metal ions and the ligand cavity. All of the manganese(II) complexes were five coordinate with exception of the acetate complex which was six coordinate. The five coordinate complexes had approximately square pyramidal geometry around each manganese(II) ion and in the six coordinate structure the geometry was still square pyramidal with the axial acetate group acting as a bidentate ligand. The difference in the structures is due to a combination of stereochemical preferences and ionic size, with the smaller nickel ion (0·83 Å) being accommodated within the plane of the molecule and adopting its preferred octahedral coordination. High spin (d^5) manganese(II) has no stereochemical preferences and with its larger radius (0·97 Å) is less easily accommodated and the metals are displaced 0·77 Å either side of the macrocyclic plane. All the nickel complexes had octahedral or tetragonal geometry. When exposed to atmospheric oxygen the manganese compounds exhibited a colour change (from yellow to dark brown) consistent with oxidation from Mn(II) to Mn(III) but these compounds were not isolated and characterised. However, the EPR spectrum of the manganese(II) acetate complex showed features that could be attributed to a partially oxidised Mn(II)Mn(III) species. The main feature of this spectrum consisted of a Mn(II) six-line hyperfine spectrum centred at $g = 2{\cdot}0$ with a spacing of 90 G, with ten weaker lines interspersed between them. This is similar to spectra for mixed valence Mn(II)Mn(III) complexes of related ligands[158]. Electronic spectra and magnetic susceptibility data indicated the presence of high spin d^5 ions in the manganese complexes. The chloride and azide complexes of manganese(II) had magnetic moments slightly lower than expected (5·83 B.M. per Mn) possibly attributable to a diamagnetic impurity or some ferromagnetic coupling. The latter is supported by the fact that the effective magnetic moment increases slightly with decreasing temperature similar to interactions reported by Hendrickson[144] and Tuchagues[34] in analogous complexes and ascribed to coupling via the phenoxy bridges. The nickel compounds exhibited antiferromagnetic coupling.

Copper(II) salts were used in the template condensation of the **LV3** and the related 2,6-diformyl-4-*tert*-butylphenol **LV3t** ligand system, in methanolic or ethanolic solution, to produce a series of 20-membered macrocyclic complexes $[Cu_2(H_2\mathbf{LV3/t})(X_2 \text{ or } SX)]^{n+}$ (X = NO_3^-, ClO_4^-, Cl^-, or NCS^-, and S = H_2O or CH_3OH).[46] Again, this series of [2 + 2] ligands did not involve endogenous alkoxy and phenoxy bridges simultaneously and did not accommodate more than two metal centres undoubtedly because of the small cavity size. These dinuclear complexes were also prepared by transmetallation, using appropriate copper(II) salts, of the comparable Pb(II) and Ba(II) macrocycles.

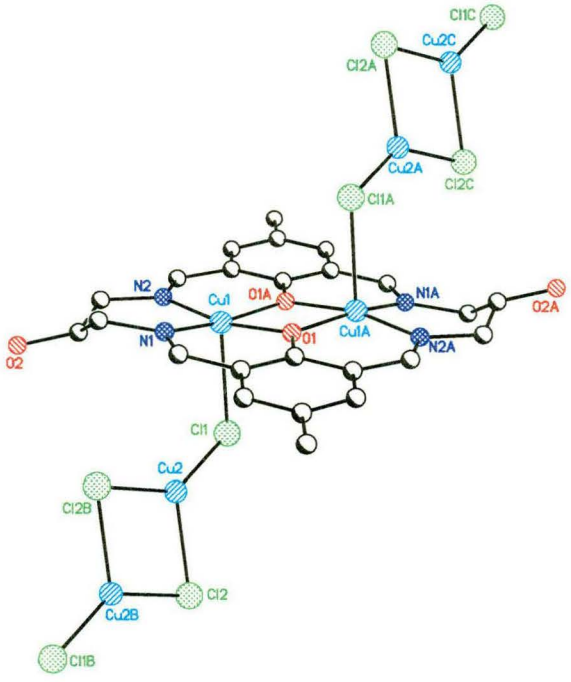


Figure 46 : Structural representation of a fragment of the $\{[Cu^{II}_2(H_2LV3)][Cu^{I}_2Cl_4]\}_n$ polymer.

The use of copper(II) chloride as the templating agent with **LV3** led to the formation of a polymeric product of undefined composition. The use of the copper(I) chloride salt produced an unusual polymer of macrocyclic copper(II) complex cations bridged axially by a $Cu_2Cl_4^{2-}$ species, which has a dinuclear chloro-bridged structure (Fig. 46). In this reaction the oxidation of copper(I) chloride to give the mixed-oxidation-state $\{[Cu^{II}_2(H_2\mathbf{LV3})][Cu^{I}_2Cl_4]\}_n$ species must involve molecular oxygen.

The reaction in the presence of copper(II) acetate and excess azide produced another polymeric copper(II) complex in which the cations were linked with $Cu_2(N_3)_6$ units. The structural and magnetic properties of the cations were comparable to similar complexes involving non-alcoholic bridging groups. However, extended magnetic interactions were observed in the azide derivatives in which intra-ring antiferromagnetic exchange and independent exchange within the dimer were accompanied by extended, antiferromagnetic interdimer exchange.

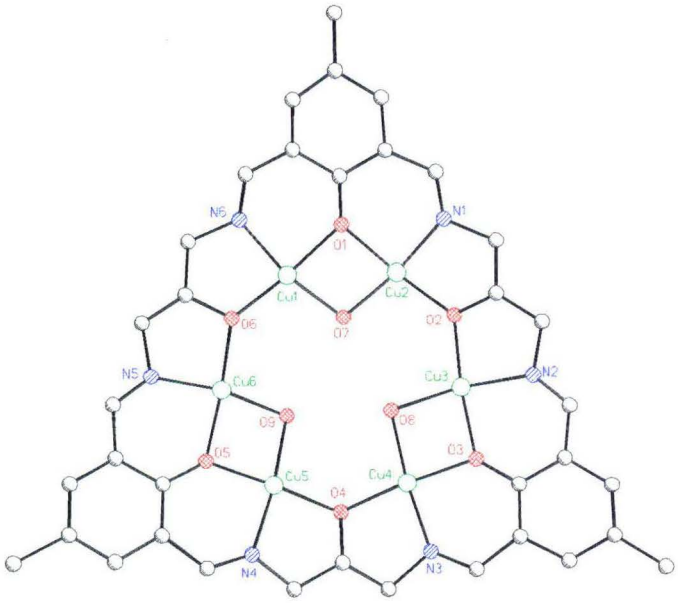


Figure 47

The [3 + 3] macrocycle derived from 2,6-diformyl-4-methylphenol or 2,6-diformyl-4-*tert*-butylphenol with 1,3-diaminopropan-2-ol[49] shows both phenoxide and alkoxide bridging and accommodates six metal atoms. The copper containing complex (Fig. 47) contains a pseudohexagonal "benzene-like" arrangement of the metal centres which are linked by alternating double (μ_2-phenoxide, μ_2-hydroxide) and (μ_2-alkoxide) bridges within each ring.

1·3·2 : 1,5-Diaminopentanol

The introduction of 1,5-diaminopentan-3-ol to this ligand system showed that the side chain length was critical in determining the nuclearity of the final product. If 1,3-diaminopropan-2-ol was used only binuclear complexes were

formed, but the use of 1,5-diaminopropanol opened the way to tetranuclear products in which the alcohol groups were now involved in the coordination sphere. M^{c}Kee first reported using the [2+2] tetranucleating macrocyclic ligands **LV5**[44] and **LV5t**[45] derived from the condensation of 1,5-diamino-pentanol and 2,6-diformyl-4-methylphenol or its 2,6-diformyl-4-*tert*-butylphenol analogue. This macrocycle is constructed of two distinct sections; the rigid phenoldiimines and the alcohol-containing side chains which impart enough flexibility into the system to permit some response to the coordination preferences of the different metal ions.

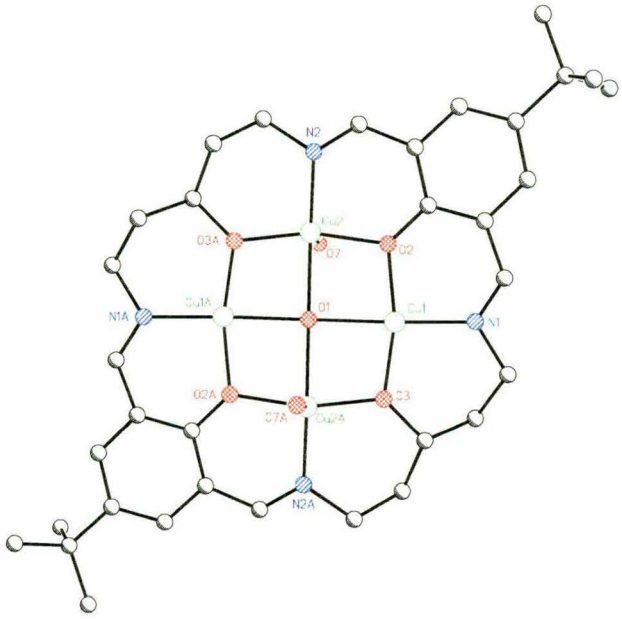


Figure 48 : The $[Cu_4(\mu_4\text{-OH})LV5t]^{3+}$ cation

Seven tetracopper(II)[43,44] (e.g Fig. 48) and three octacopper complexes[43,45] of **LV5** and **LV5t** were reported. The alcohol and phenol groups of the macrocycle were all deprotonated and each bridged two copper ions; so that the ligand was octadentate. The tetranuclear complexes contained planar $Cu_4(\mu_4\text{-OH})$ cores but in one variation the hydroxo donor has been displaced by two azido groups to form a complex in which the four copper(II) atoms are no longer coplanar. A planar Cu^{II}_4OH core had been seen in the complex $[Cu^{II}_4\mathbf{LFAb}(\mu_2\text{-OH})(CH_3CN)_2]\cdot(ClO_4)_2$ derived from the [2 + 2] condensation of 2,5-diformylfuran with 1,2-bis-(aminomethyl)-benzene[159] but in this complex the μ-OH was disordered and only associated with two of the Cu at a time. In non-

protic solvents or with added base, the tetracopper(II) complexes dimerise with the loss of the hydroxo proton to form octacopper complexes containing two $Cu_4(\mu_4\text{-}OH)$ units.[45] The exposed copper-oxygen array, with metal-metal distances of ~ 3 Å, is reminiscent of a metal oxide surface and this prompted the researchers to look at the binding of substrates to the open faces of these structures.

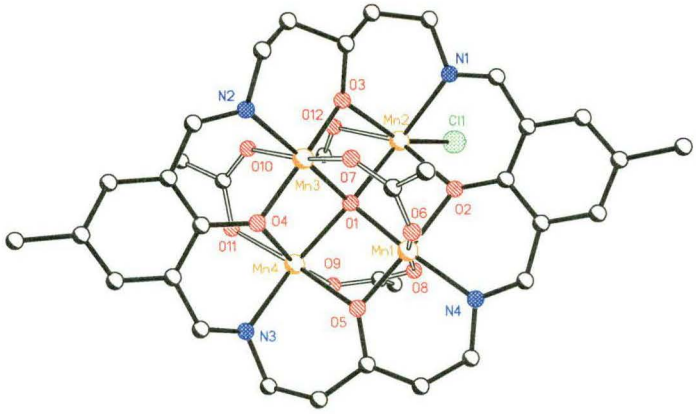


Figure 49

The $[Mn_2^{II}Mn_2^{III}(\mu_4\text{-}O)$**LV5**$(CH_3COO)_3Cl(CH_3OH)]\cdot 3CH_3OH$ complex (Fig. 49) of this system[47] the macrocycle was shown, by X-ray techniques, to be non-planar. In contrast to the planar tetracopper(II) complex prepared from H_4**LV5**[44] the mean planes of the two phenol rings are inclined to each other at an angle of 38·5° (Fig. 50). As in the copper complexes all of the phenol and alcohol groups are deprotonated and each bridges two manganese ions, so that the ligand is octadentate.

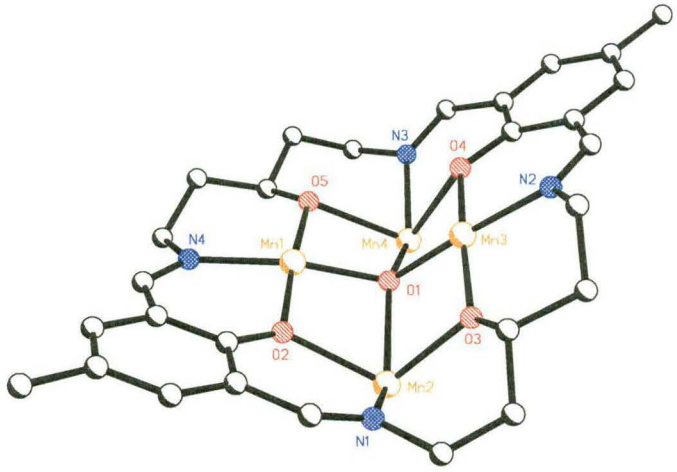


Figure 50 : Showing the twisted nature of the macrocyclic core.

The stoichiometry of this complex indicated an average oxidation level for each manganese ion of 2·5 but structural data provided strong evidence for the localisation of the charges as bond distances around two of the manganese atoms, Mn1 and Mn2 (assigned +3 oxidation level)(Fig. 50), are very similar and significantly shorter than the equivalent bonds to the other two (assigned +2). Similar distinctions in bond lengths had been reported in other $Mn^{II}Mn^{III}$ mixed-valence systems.[34, 160] The most likely oxidising agent for this process was molecular oxygen and it was considered to be the source of the oxo-ligand.

The mean magnetic moment fell from 5·12 B.M. per Mn (300K) to 4·56 B.M. per Mn (93K) indicating the presence of electronic interactions between the metal ions as both of these measurements are below the spin only moment expected in the absence of coupling i.e. 5·41 B.M. per Mn. Preliminary ESR spectra showed the 6-line spectrum expected for Mn(II) but there was an underlying spectrum which may have been attributable to the tetramer. It was thought that the facile oxidation of two of the metal centres meant that other oxidation levels should be accessible for this complex and it was expected the presence of the macrocyclic ligand bound to the four metal ions would assist in maintaining the structure intact in solution and through chemical changes.

1·3·3 : 2,6-bis(aminomethyl)-4-methylphenol

The [2 + 2] condensation, by Robson *et. al.,* of 2,6-diformyl-4-methylphenol with 2,6-bis(aminomethyl)-4-methylphenol produced a new Schiff base ligand **LAmP**. In contrast to M^{c}Kee's tetranuclear copper complexes Robson's arrays are not planar but adopt a bowl shape. This ligand system, having four phenol units interconnected by carbons ortho to the hydroxyl groups, is reminiscent of the calixarenes. This is especially true of the bowl-shaped structures of some of the derivatives of the reduced form (refer p. 58). It has been suggested that ligands capable of binding four metals in close proximity, in such a way that they had a central cavity accessible to substrate molecules, might lead to new complexes with unprecedented structures and reactivity. This group hoped to create circumstances in which molecules were trapped with unusual bonding

which might lead to their consequent activation, multi-electron reduction or oxidation of the substrates, and new types of reactions between species attached to the neighbouring metal centres. [3 + 3] and [4 + 4] macrocyclic complexes have also been achieved with this system. The diprotonated metal-free macrocyclic derivative (H_6**LAmP**)(BF_4) was formed by adding excess HBF_4 to a methanolic solution of the zinc complex.

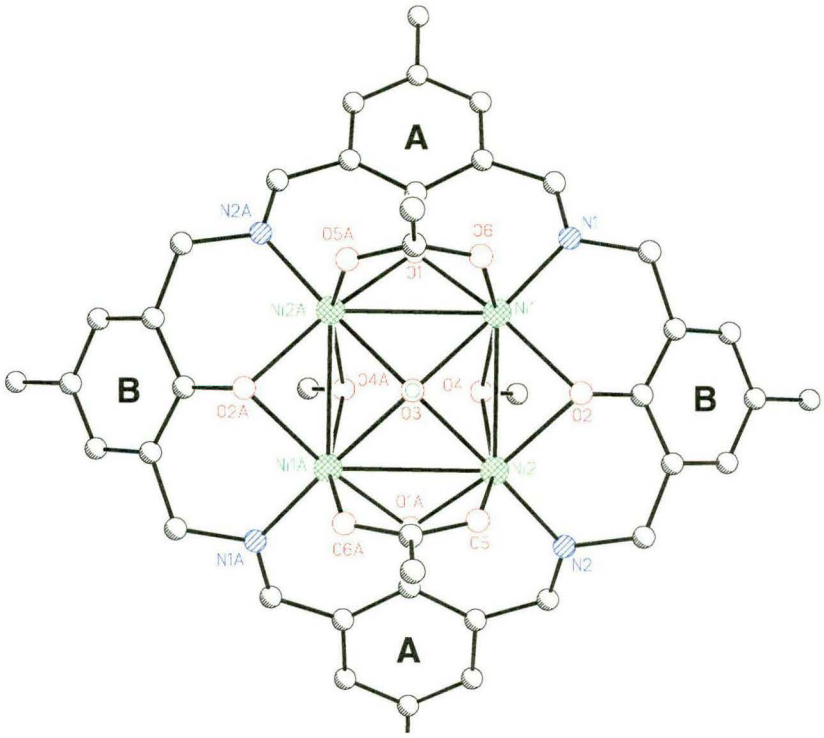


Figure 51 : The tetra-nickel cationic core of LAmP

In the complex [Ni_4**LAmP**(CH_3CO_2)$_2$(μ_4-OH)($CH_3O{\cdot}H{\cdot}OCH_3$)] $4CH_3OH$[61,62] four nickel(II) ions are bound at the corners of an approximate square (Fig. 51) with an edge of 2·8 - 2·9 Å. The four aromatic rings are inclined, all on the same side of the Ni_4 plane, to form a bowl-shaped molecule (Fig. 52). The dihedral angle between this plane and the aldehydic (A) phenol rings was 34·6° and those between the plane and the amino(B)-phenols was 38·3°. Two acetate and two methoxo bridges link the nickels on this side of the plane and, on the opposite side of the plane, two more acetates bridged the nickels associated with the phenoxide residues in ring A. A μ_4-OH, was associated with all four nickels; the hydrogen on this oxygen was clearly seen between the two methoxo units and hydrogen bonded to the methoxo oxygens to give a $(CH_3O{\cdot}H{\cdot}OCH_3)^-$ system with a very short oxygen-oxygen separation of

2·509(7) Å. The oxygen centres of the phenoxide residues in B and the methoxo units were pyramidal (i.e. 0·67 Å out of the plane of its bonded neighbours) whereas the phenoxide residues of A were almost planar. The pseudo-octahedral arrangement around each nickel ion was completed by the μ_4-OH group the oxygen of which was ~0·60 Å above the midpoint of the Ni_4 cluster and equidistant from all four metals.

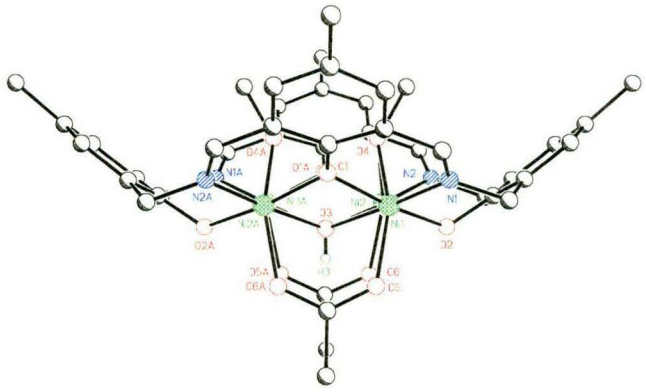


Figure 52

Replacement of the acetato ligands in this complex[161] with either azide or methoxide gave derivatives which X-ray studies revealed contained the intact $[Ni_4$**LAmP**$(\mu_4\text{-OH})(CH_3O{\cdot}H{\cdot}OCH_3)]^{2+}$ core present in the acetato complex. In these new complexes the short O·····O distances of the unusually strongly hydrogen-bonded $(CH_3O{\cdot}H{\cdot}OCH_3)$ unit were 2·492(7) Å for the azido and 2·42(1) Å in the methoxo complexes (Fig. 53). An interesting feature of the azido complex was that it had no uncoordinated solvent molecules in the crystal, allowing efficient crystal packing to be achieved by hydrogen bonding interactions between a coordinated water of one molecule and the pyramidal phenolic oxygen of another.

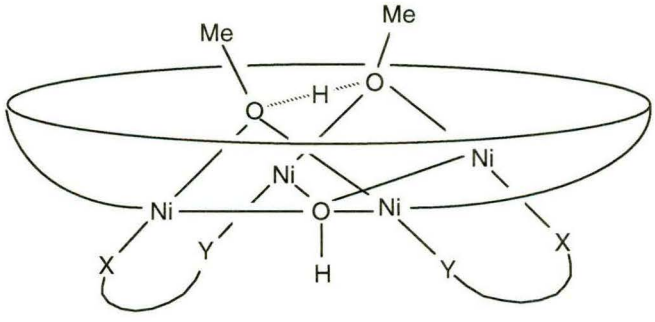


Figure 53 : The bowl-like $[Ni_4(LAmP)(\mu_4\text{-OH})(CH_3O{\cdot}H{\cdot}OCH_3)]{\cdot}2XY$ structure common to the acetato [XY = CH_3COO^-], the azido [XY = H-bonded $(N_3{\cdot}H{\cdot}OH)^-$] and the methoxo [XY = $(CH_3O{\cdot}H{\cdot}OCH_3)^-$] complexes.

The three nickel(II) complexes showed very similar magnetic properties (300 - 4·2 K), with the Ni_4 group behaving as a noninteracting pair of Ni_2 units within which there was an antiferromagnetic coupling with J values -33·3 cm^{-1} (acetato), -28·5 cm^{-1} (azido), and -30·0 cm^{-1} (methoxo); this suggested that the common core was little influenced by the exogenous ligands. The coupled pairs were thought to be those involving the dialdehyde-derived phenoxide bridges, which were essentially trigonal. The dialdehyde imine components (i.e. those encompasssing Ni1, Ni2A and Ni2, Ni1A in Fig. 51) provided an essentially coplanar coordinating environment with a trigonal-planar phenolate O2 oxygen bridging atom, a situation known in the related binuclear nickel macrocyclic systems of $[Ni_2$**L3-3**$Cl_2]\cdot 2H_2O$ (J = -27 cm^{-1})[134] and $[Ni_2$**L3-3**$(py)_4]\cdot(BF_4)$ (J = -23 cm^{-1})[108] to provide antiferromagnetic exchange very similar to that observed here and independent of ligand variations. It was thought that future investigations should concentrate on the "equatorial" bridging groups between the Ni atoms as these would provide the most important superexchange pathways between the $d_{x^2-y^2}$ orbitals of the S = 1 Ni^{II} centres.

The zinc(II) complex Zn_4**LAmP**$(CH_3CO_2)_3(\mu_4\text{-}OH)2\cdot 64CH_3OH\cdot 2\cdot 5H_2O$[61] of this macrocycle had a similar, but less bowl like, ligand arrangement. The phenol rings were all inclined on the same side of the Zn_4 cluster but at four different angles to the mean plane through the metals - 33°, 58°, 39°, and 23°. The Zn_4 group was markedly distorted from a square having one short and one long diagonal (~ 3·6 and 4·7 Å respectively) and no longer being planar. One zinc was between 4- and 5-coordinate, two were 5-coordinate and the fourth was 6-coordinate.

Robson's team went on to investigate the reduced form of this ligand[162,163] as this form was thought to be more robust to harsher reactivity studies. It was considered that reactions which readily occur at the CH=N links, *e.g.* hydrolytic disruption of the ligand, were less likely to affect CH_2–NH bonds and this proved to be the case. One of the features desirable in a polynuclear metal complex, which is intended to catalyse some multistep reaction of substrates, is

sufficient flexibility to allow metal-metal spatial relationships and individual metal coordination geometries to vary from one intermediate to the next as substrates are introduced, modified and finally expelled. From this point of view, it was considered that the more flexible reduced system, **LAmP$_R$**, may have distinct advantages in much the same way as **L3-3$_R$** has over **L3-3**. The dihydrochloride derivative of H_4**LAmP** was reduced by excess sodium borohydride in ethanol at 0ºC to the tetra-amino macrocycle **LAmP$_R$** which was isolated, stored and used to synthesise complexes, as its tetrahydrochloride salt. Single crystals of the reduced ligand with the interesting solvent composition [(**LAmP$_R$**)·4HCl·H_2O· CH_3OH·C_2H_5OH] were obtained from an undried methanol-ethanol mixture acidified with HCl gas (Figs. 54a & 54b).

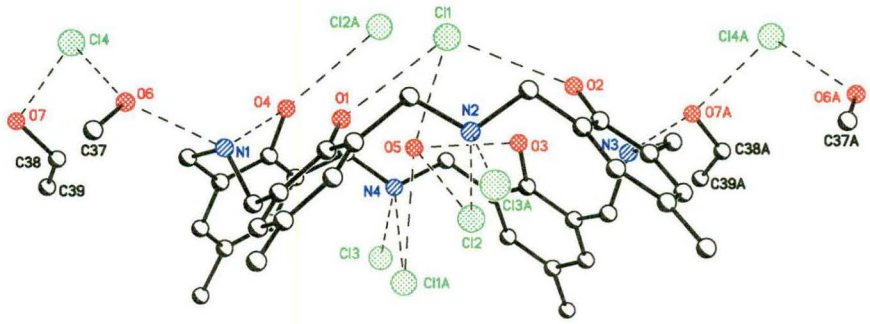


Figure 54a

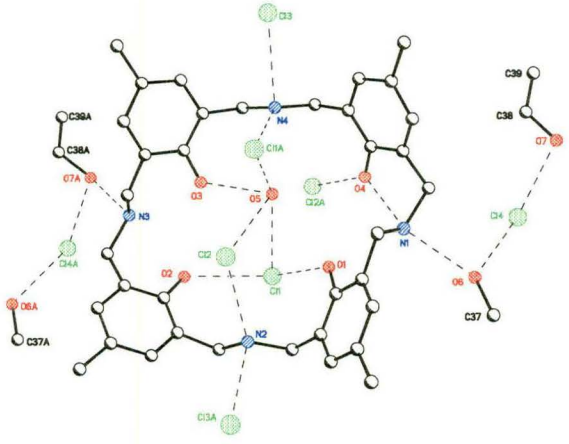
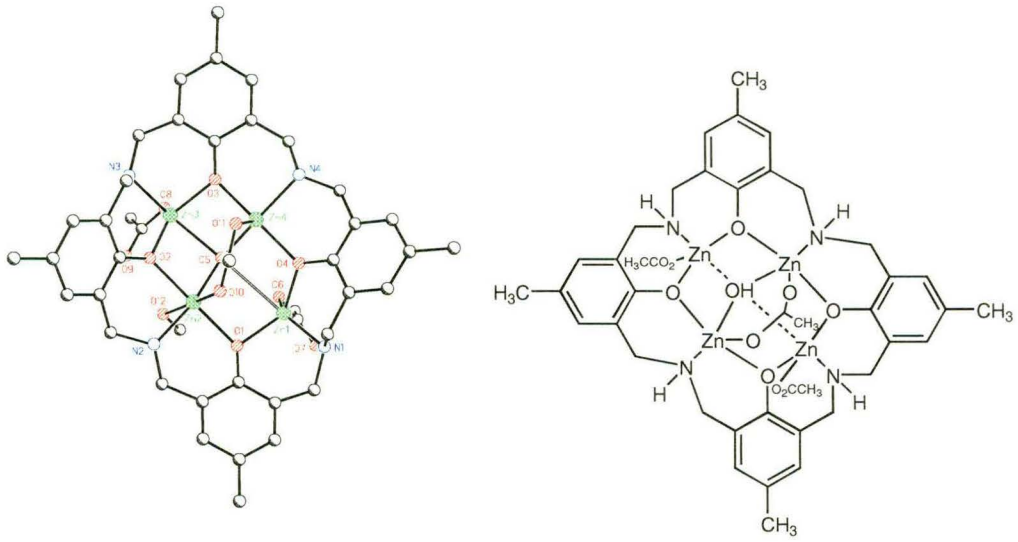


Figure 54b

A tetra-zinc(II) complex, [Zn^{II}_4(μ_4-OH)(**LAmP$_R$**)(CH_3CO_2)$_3CH_3OH$]·1·5CH_3OH of the reduced ligand was very similar to the Schiff base analogue with the four zinc centres being not quite as coplanar and one of the rhombus diagonals

being more elongated (~ 5·11 and 3·5 Å respectively) into somewhat of a kite shape. (Fig. 55a) The μ_4-OH was still centrally placed but was not bonded equally strongly to all four metal centres and was 2·849(5) Å from the fourth zinc. If this interaction was ignored then this zinc had irregular 4-coordinate geometry, two zincs were 5-coordinate and the other was 6-coordinate. ^{13}C and ^{1}H NMR spectra of the tetrazinc complex in $CDCl_3$ showed that the solution species underwent rapid interconversion to produce an averaged arrangement with C_{2v} symmetry (Fig 55b).



a **b**

Figure 55 : a : $[Zn^{II}_4(LAmP_R)(CH_3CO_2)_3(\mu_4\text{-}OH)CH_3OH]$
b : Averaged arrangement of the Zn_4LAmP_R complex, with C_{2v} symmetry, in solution.

The incorporation of B_2O and CH_2 into the reduced ligand gave two other extremely interesting derivatives of this system. **LAmP**·2HCl was obtained, as orange crystals, from a mixture of 2,6-diformyl-4-methylphenol, 2,6-bis(amino-methyl)-4-methylphenol and acetic acid maintained just below boiling point in a methanolic solution. The crystals would start to separate after two hours. If this solution was cooled to ice temperature and treated with excess sodium boro-hydride just before the solid started to appear, a different colourless crystalline solid was formed.[163] The elemental composition and FAB mass spectrum of this material supported the formulation of **$LAmP_R$**·B_2O. The formation of cyclic bezoxaborines when Schiff bases of salicylaldehyde derivatives are reduced with sodium borohydride had been reported previously.[164] The structure shown in the diagram (Fig. 56a) was considered to be much more likely than one in

which the borons were in adjacent sites as this would have to contain a strained 4-membered B_2O_2 ring. This conjectured structure was later supported by the X-ray characterisation of a number of binuclear derivatives of **LAmP$_R$** with metals in diagonally opposite nucleation sites.[165]

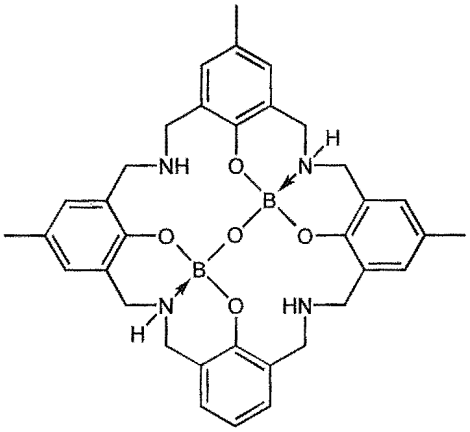


Figure 56a

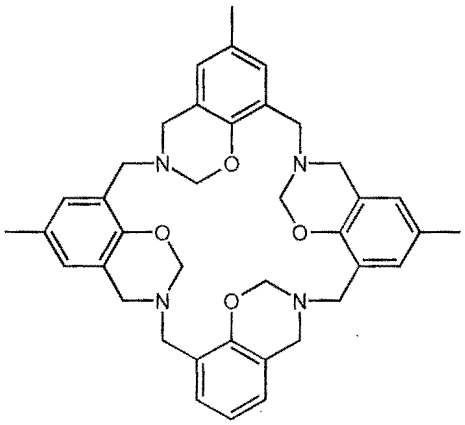


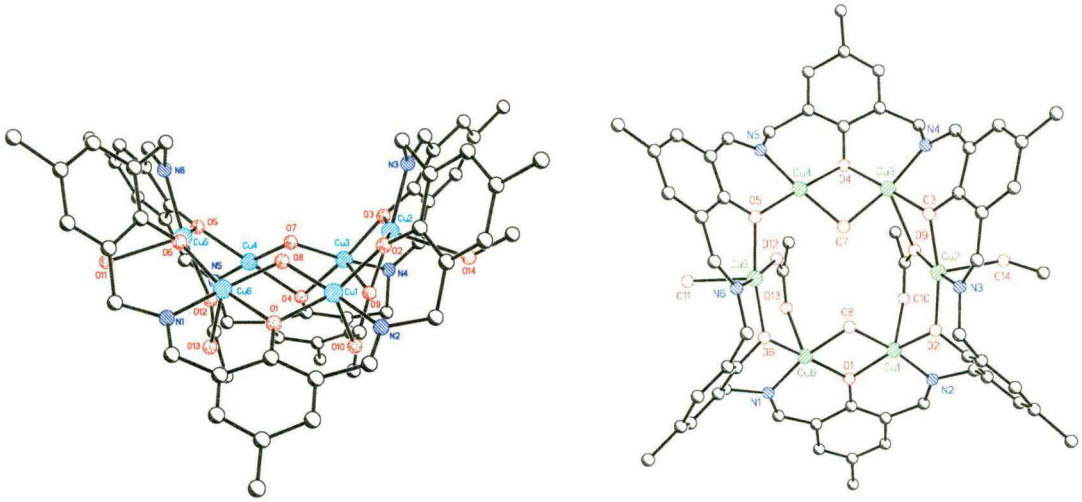
Figure 56b

Robson and his researchers were interested in the reaction between the **LAmP$_R$** ligand system and formaldehyde for two reasons: firstly an interest in just how many of the nucleation sites could be occupied by carbon centres and secondly the possibility of a different method of synthesis of this ligand or a convenient derivative of it. It was thought that maybe it was accessible by a Mannich related condensation of the inexpensive and readily available starting materials *p*-cresol, formaldehyde and ammonia. The reaction of **LAmP$_R$**·4HCl with formaldehyde and lithium acetate gave **LAmP$_R$**·4CH_2[163] which was characterised by elemental analysis, MS, and IR and NMR spectroscopy. (Fig 56b) Treatment of the CH_2 and B_2O complexes with aqueous ethanolic HCl returns them to the starting material **LAmP$_R$**·4HCl.

The reaction between 2,6-diformyl-4-methylphenol, 2,6-bis(aminomethyl)-4-methylphenol, copper(II) acetate, and tetrabutylammonium tetrafluoroborate (1:1:2:excess) in methanol, gave the first example* in which a single macrocyclic ligand bound six metals in close proximity.[63] This [3 + 3] condensation gave the complex $[Cu_6(\mu_2\text{-}OH)_2$**LAmP3**$(CH_3COO^-)_2(CH_3OH)_2H_2O]\cdot(BF_4)_2 \cdot 4\cdot 4CH_3OH$ in which **LAmP3** is a macrocyclic hexa-Schiff base hexaphenolate

* This reaction was carried out in 1990 before the already discussed complexes of Thompson *et.al.*[49] were synthesised.

ligand (Fig. 57). The complex binds the six copper(II) ions in a boat arrangement with two μ_2-hydroxo groups (O····O separation 3·32 Å) occupying the central cavity.



a b

Figure 52 : a : The coordination environment of the Cu_6 core showing the boat arrangement adopted by the metal atoms. b : The $[Cu_6(LAmP)_3\,CH_3COO^-)_2(\mu_2\text{-}OH)_2(CH_3OH)_2{\cdot}H_2O]^{2-}$ cation.

1·4 : N-containing lateral chains

Kahwa[166] reported the first homodinuclear lanthanide complexes of **LN2** formed from the [2 + 2] condensation of 2,6-diformyl-4-methylphenol and 1,8-diamino-3,6-diazaoctane (trien)(Fig. 58a). It was felt that homodinuclear lanthanide complexes could provide information regarding $Ln^{3+} - Ln^{3+}$ interactions, crucial to the scientific understanding and technological applications of the rare earths. He noted that, although macrocyclic or macroacyclic complexes would seem appropriate for these studies, only heterodinuclear or mononuclear [1 + 1][167] complexes had been achieved. The fact that similar complexes could not be achieved with the diformylpyridine head-unit suggested that is was a strong interaction between the phenolate anion and the Ln^{3+} cations that offset the Ln^{3+} - Ln^{3+} repulsive interactions. These complexes showed predominant ligand-to-Ln^{3+} energy transfer processes and significant $Ln^{3+} - Ln^{3+}$ antiferro-magnetic coupling[168] indicating phenol bridging between the metals. This was unable to be confirmed by X-ray analysis.

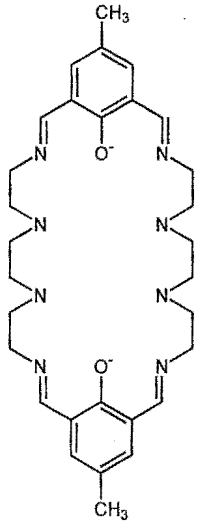


Figure 58a : LN2

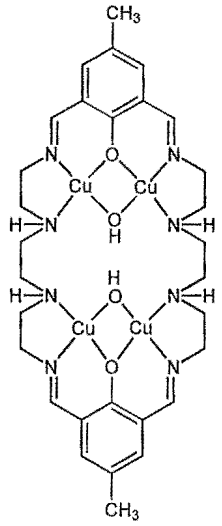


Figure 58b

Okawa *et. al.*[41] condensed 1,8-diamino-3,6-dialkyl-3,6-diazaoctane (alkyl = methyl or ethyl) with 2,6-diformyl-4-methylphenol to produce the [2 +2] macrocycles **LN2m** and **LN2e**[*]. With the hope of modeling the OEC of Photosystem II he had the intention of preparing a "dimer of dimers" type tetranuclear manganese complex in which two OH^- (or O^{2-}) groups, each bridging a pair of manganese ions, would be facing each other in close enough proximity to provide a stereochemical pathway for O-O bond formation. From the H_2**LN2** ligand Okawa had prepared a tetranuclear copper(II) complex, $[Cu_4$**LN2**$(OH)_2](ClO_4)_4$, (Fig. 58b) in which a pair of copper(II) ions was bridged by a phenolic oxygen and in which two bridging OH^- groups faced each other at a close distance[32], but attempts to prepare a similar tetranuclear manganese complex by the same method were not realised. In related reactions using 1,9-diamino-3,7-diazanonane and Pb^{II} as the template ion, a ring-contraction condensation through the two secondary amino groups of the tetraamine and one formyl group of 2,6-diformyl-4-methylphenol yielded the macrocycle **LN3** (Fig. 59) which incorporated hexahydropyrimidine rings.[169] Kahwa had earlier reported that when 2,6-diformyl-4-methylphenol, trien and praseodymium(III) or neodymium(III) salts are used in a similar reaction, a [3 + 1] condensation occurs to produce complexes of **LN4** which contain an imidazoline ring (Fig. 60).[170]

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[*] **LN2m** and **LN2e** are variations of the LN2 macrocycle having methyl and ethyl substituents on the nitrogen atoms of the side chains.

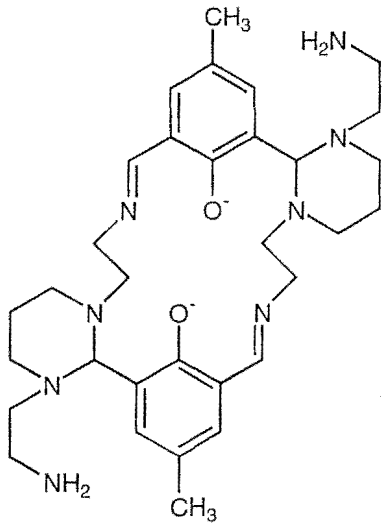


Figure 59 : LN3

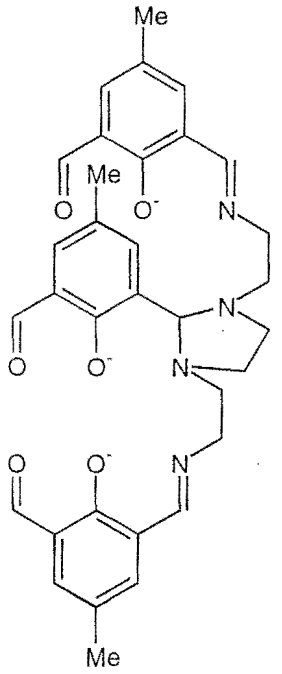
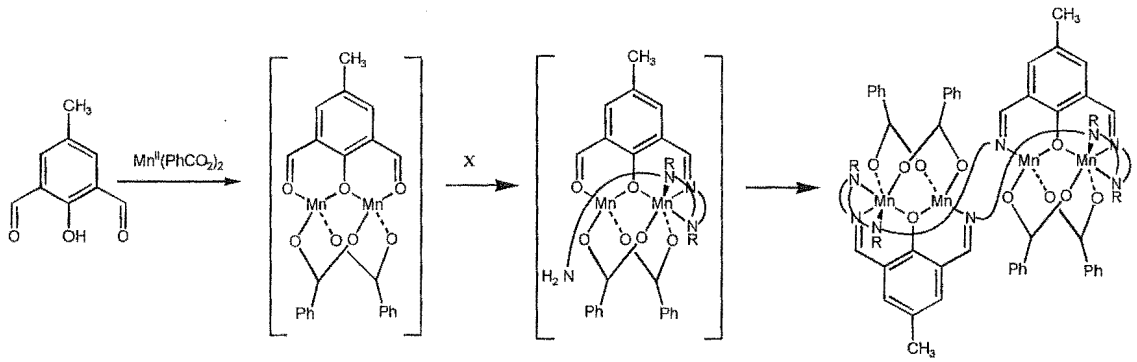


Figure 60 : LN4

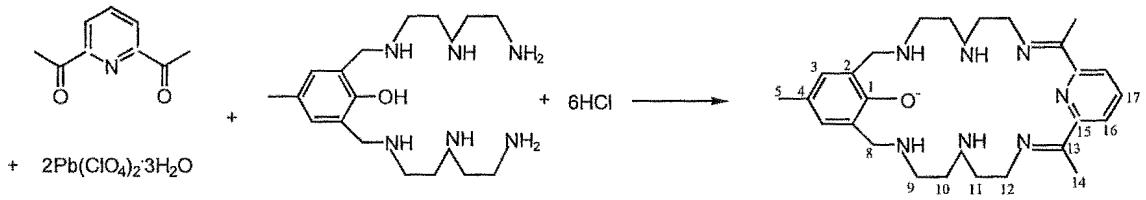
Since it was considered that the ring contraction was the result of using trien and Mn(II) as the templating ion, it was decided to use the alkyl derivatised analogues of trien and in preliminary studies a dilead(II) complex of **LN2m** was obtained. The template reaction of 2,6-diformyl-4-methylphenol and 1,8-diamino-3,6-dialkyl-3,6-diazaoctane with manganese(II) benzoate tetrahydrate (1:1:2) gave the tetranuclear complexes $[Mn_4(\mathbf{LN2m/e})(PhCO_2)_6]$ and the structure of $[Mn_4(\mathbf{LN2m})(PhCO_2)_6(Me_2CHOH)_2]\cdot 2CH_2Cl_2$ was determined by single-crystal X-ray diffraction. The order of mixing of the starting materials in this template synthesis was crucial to its success. If the manganese(II) benzoate and the diamine were mixed first in methanol and then the 2,6-diformyl-4-methylphenol added no complex was obtained from the resulting red-brown solution. The same reaction under anaerobic conditions gave orange solution from which the desired products were not obtained. When the manganese salt and 2,6-diformyl-4-methylphenol were mixed first in methanol and the tetraamine added to this mixture under aerobic conditions the reaction mixture was orange and the macrocyclic complexes formed in good yield. Based on these facts and the confirmed structure of the complexes a proposed mechanism for the formation of these complexes is shown in Scheme 2. It appears that the air-stable μ-phenoxo-bis(μ-benzoato) dimanganese(II) core forms first and, upon treatment with the amine, a [1 + 1] complex in which one

of the formyl groups and one of the primary amine groups remain intact is achieved. Dimerization of this intermediate gives the tetramanganese(II) product. Magnetic measurements showed that the two dimanganese(II) units in the molecule were magnetically independent of each other and that a weak antiferromagnetic interaction operated within each μ-phenoxo-bis(μ-benzoato)dimanganese core(II). The exchange integrals were similar to those found for other complexes with this core.[171,172]



Scheme 2 : Mechanism for the formation of complexes LN2m and LN2e. (X) = $H_2N{\cdot}(CH_2)_2{\cdot}NR{\cdot}(CH_2)_2\ H_2N{\cdot}R$ = Me or Et

An unsymmetrical ligand system, which provided two distinct metal binding sites, was designed by Brooker.[173] Since macrocycles incorporating three or more metal ions were rare it was hoped to develop trimetallic complexes. The approach was to form an unsymmetrical dilead(II) complex, by first forming the three-quarter macrocycle, Scheme 3, partially neutralising this macrocycle, then reacting it with 2,6-diacetylpyridine, and KOH in the presence of lead(II) perchlorate in refluxing methanol to yield the complex $\{[Pb_2(\mathbf{LN5})Cl](ClO_4)_2\}_x$.



Scheme 3

Single crystal X-ray analysis (Fig 61) revealed that this complex is part of a polymeric chain with the macrocyclic moieties linked by chloride ions. There is distorted six-coordinate geometry and chemically similar coordination environments about both lead ions. Each is bridged by the phenolic oxygen

atom and is bound to an imine nitrogen, two amine nitrogens, a chloride ion and weakly by the bridging pyridine nitrogen. This bridging mode of the pyridine is extremely rare with very few being structurally characterised.[174]

Transmetallation with transition metal salts has yielded a copper complex, the structure of which, based on FAB-ms data and elemental analysis, is proposed to be trinuclear.

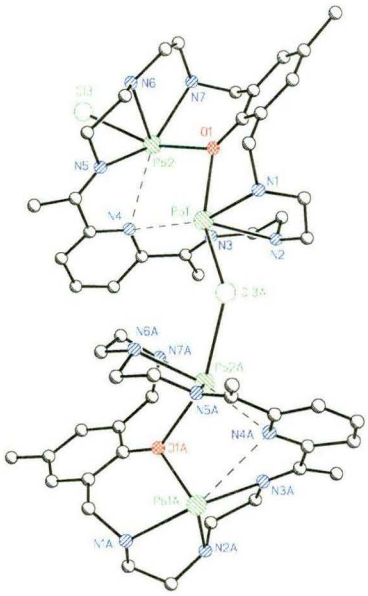


Figure 61

Thompson *et. al.*,[50,51] included sulphur donors in the N-containing lateral chains they used. (Fig. 62)

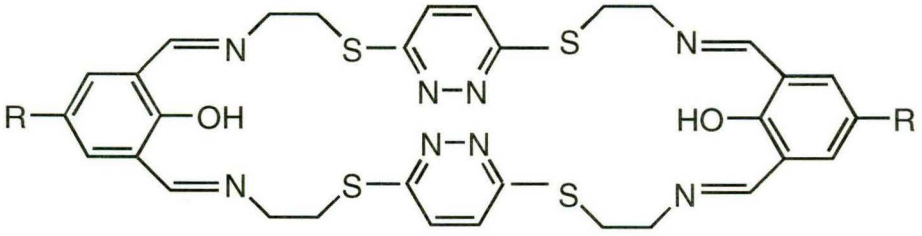


Figure 62 : LNSm (R = methyl) or LNSt (R = *t*-butyl)

The template condensation of 2,6-diformyl-4-methylphenol (**LNSm**) or 2,6-diformyl-4-*tert*-butylphenol (**LNSt**) and 3,6-bis((2-aminoethyl) thio)pyradizine (1:1) in the presence of copper(II) salts gave a series of four copper(II)

complexes which included mono-, di- and tetranuclear complexes. The latter involve a dimerisation of two dinuclear halves, with an unusual combination of μ_2-anion and/or μ_3-alkoxy bridges. The incorporation of longer diamine fragments, with additional donor alcohol groups, e.g. 1,3-diamino-propan-2-ol, 1,5-diaminopentanol, and 2,6-bis- (aminomethyl)-4-methylphenol, had increased the coordination capacity of the resulting macrocycles and led to the formation of complexes with four and even six metals accommodated within the macrocyclic ring. It was hoped that 3,6-bis((2-aminoethyl)thio)pyridazine would do the same since it was potentially decadentate (N_8O_2).

The involvement of the sulfur atoms as donors could have increased the coordination capacity beyond four metals. However, use of copper(II) salts with weakly coordinating or noncoordinating anions, such as BF_4^- and ClO_4^-, produced dinuclear derivatives in which the two distorted copper(II) centres were bound in the familiar diphenoxide bridged structure with in-plane imine donors. The organisation of the two phenoxide units about the dinuclear centre involved the ligand in a most unusual twist, of approximately 150º, in which the pyridazine fragments looped over the copper atoms on either side of the dinuclear centre and had weak axial coordination to them.[50] This twist causes considerable distortion at the copper centres (Fig. 63).

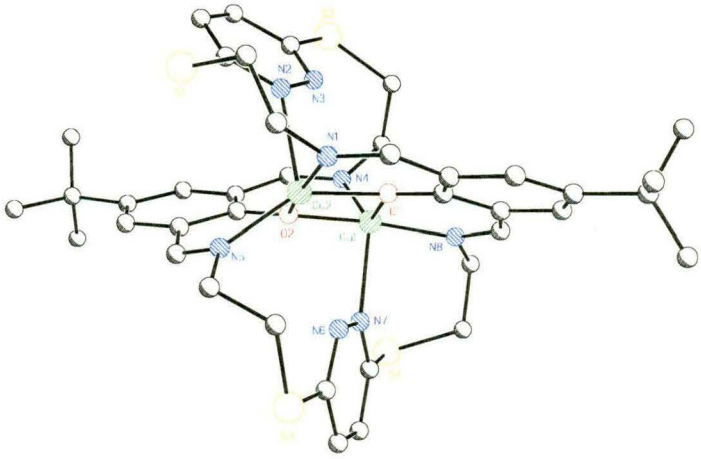


Figure 63: The dicopper complex of LNSt

Consideration of the formation of these complexes gives a possible explanation of the source of this ligand twist. Initially the 2,6-diformyl-4-R-phenol was

reacted with the copper salt in hot refluxing methanol presumably to produce a "planar" dinuclear phenoxide-bridged intermediate involving terminal aldehyde coordination (Cu_2O_6). Apparently the subsequent addition of the diamine did not complete the macrocycle by condensation of its two diamine ends on each side of the dinuclear intermediate but rather one imine end was formed and then, because of strain considerations, the other end of the diamine spanned the dinuclear centre and completed its second imine condensation at the other copper atom. This process was repeated with the second diamine to complete the macrocycle and produced an arrangement where the two diamine fragments acted as diagonal "straps" between the copper atoms.

These complexes exhibit strong antiferromagnetic coupling and spin-exchange occurs through the phenoxide oxygen bridge network, as seen in many other related compounds. Cyclic voltammetry for all the complexes was very similar and involved two quasi-reversible redox processes involving two one-electron reduction steps at negative potentials (0 to 0·7 V vs SCE). The two redox waves were very well separated and conproportionation constants were substantially larger than those reported for complexes of this sort involving simple aliphatic linkages between the imine nitrogens and copper ions with geometries much closer to square planar. Changing the aliphatic linkage from propylene to butylene led to a substantial shift of both reduction waves to positive potentials associated with enhanced molecular flexibility.

The mixed-valence (Cu(II) - Cu(I)) species were generated electrochemically and studied by EPR spectroscopy. The frozen glass (77 K) spectra of all four mixed-valence compounds were typical "axial" spectra and showed the unpaired electron to be localised on one copper centre. The copper hyperfine splittings were somewhat lower than those reported by Hendrickson[52,174] for related complexes, indicating a more pronounced tetrahedral distortion, consistent with the structural data, at the copper centres.

In contrast, if the same condensation was carried out in the presence of other copper(II) salts of anions with significant coordinating abilities (e.g. Cl, Br, NO_3, CF_3SO_3), then [1 + 1] macrocycles which accommodate two copper centres

involving phenoxide and methoxide or anion bridges are formed. The reaction of 2,6-diformyl-4-methylphenol, 3,6-bis((2-aminoethyl)thio)pyridazine, copper(II) nitrate and trifluoromethanesulfonate (triflate)[51] led to the formation of the binuclear complex $[Cu_2(\mathbf{LNSm})(\mu_2\text{-}OCH_3)(X)_2]$ where X = NO_3, CF_3SO_3. Treatment of the nitrate complex with chloride, azide, bromide and thiocyanate gave four tetranuclear dimeric compounds. Representative examples of both the bi- and tetranuclear complexes are shown in Fig. 64. When copper thiocyanate was used directly in this reaction an unexpected mononuclear complex resulted. All but the triflate complex were characterised by single crystal X-ray determination.

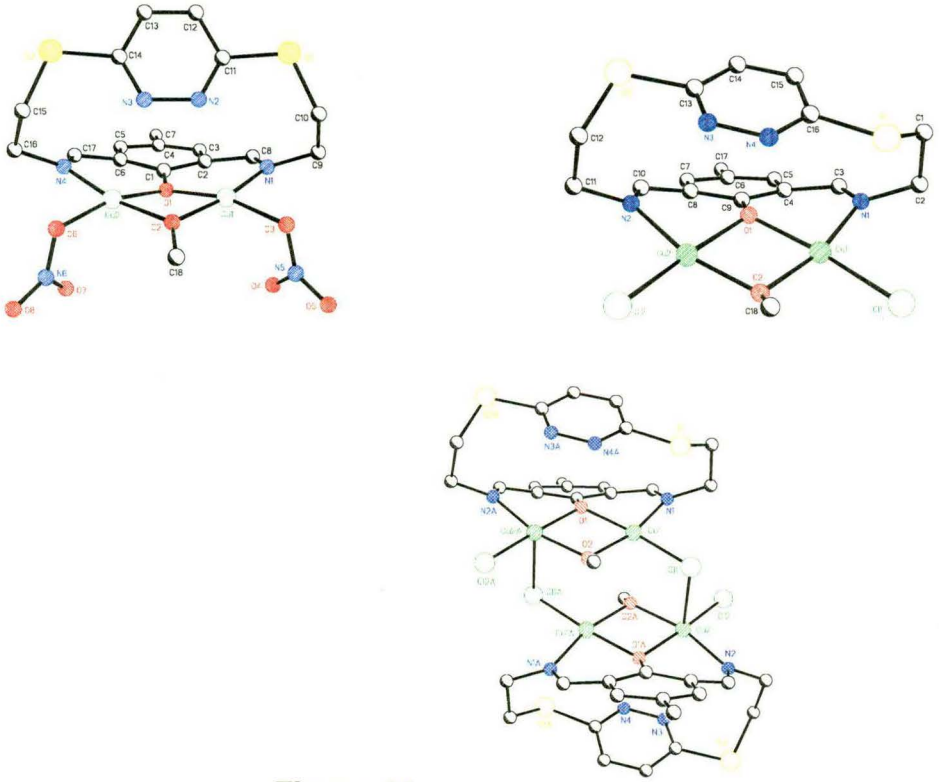


Figure 64

In the binuclear complex the two copper atoms are bridged by the phenoxide oxygen and terminally bound by an anion. Presumably this is an intermediate existing before the addition of the 3,6-bis((2-aminoethyl)thio)pyradizine which then is attacked by the coordinated aldehydic carbonyl groups and ends up, due to its flexibility, spanning the dinuclear centre in a "nonbonding" fashion. The tetranuclear complexes were made metathetically from the nitrate complex and in these two binuclear units are bridged by μ_2-anions, μ_3-methoxy or μ_3-ethoxy groups coordinated to two copper centres in each unit. The $CuCl_2$ and

$CuBr_2$ dimers could be made by direct reaction of the substrates but in both cases an unusual redox reaction occurred, to produce mixed-oxidation-state Cu(II) - Cu(I) species as the major components. The formation of alkoxide rather than hydroxide bridged complexes in these reactions was puzzling as water had not been excluded. It was thought that the highly basic nature of the diamine may have assisted in deprotonating the coordinated alcohol molecule to form a diamine salt but no such species was detected.

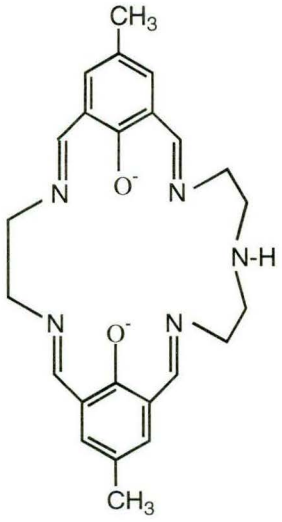


Figure 65

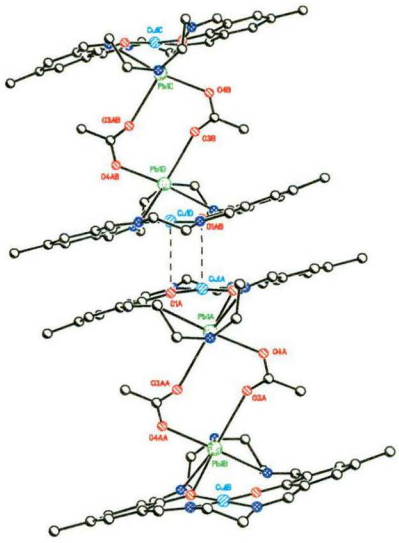


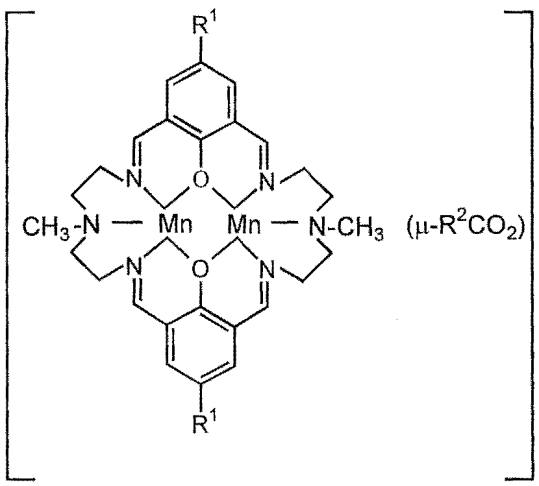
Figure 66

Very recently Okawa[39,40] has turned his attention to modifications of **L2-2** with a view to forming ligands with dissimilar coordination sites. Replacement of one lateral $-(CH_2)_2-$ chain with one $-(CH_2)_2NH(CH_2)_2-$ chain afforded the ligand **LN1** which contains dissimilar 4- and 5- coordination sites (Fig. 65). Hetero-dinuclear Ni(II)M(II) (M = Pb, Mn, Fe, Co, Ni, Cu, Zn) complexes have been formed by a stepwise template condensation reaction to produce the Ni(II)Pb(II) complex which was then used as a precursor for the rest. It was assumed that in the (NiPb) complex the Ni(II) ion was located at the 4-coordinate site and assumed an essentially planar geometry as supported by the diamagnetic behaviour of this complex. The split ν_3 band of the perchlorate group (1140, 1110, and 1080 cm^{-1})[176] indicated that the Pb(II) ion in the 5-coordination site of the macrocycle may have assumed an eight-coordinate structure as previously seen in a related (CuPb) structure (Fig. 66).[39] The NMR spectral features for

the (NiPb) complex were consistent with the X-ray crystallographic result for the (CuPb) structure.

The heterodinuclear complexes, (NiMn), (NiFe), (NiCo), and (NiCu), exhibited magnetic moments consistent with high-spin Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) complexes. The (NiZn) complex is diamagnetic. These facts indicate that the Ni(II) ion is diamagnetic in all the complexes. NMR of the (NiZn) complex indicates that in solution the 5-coordinate site is free from coordination to the Zn(II) ion. From the electronic spectra it was seen that this method of synthesis gave Ni(II)Cu(II) and Cu(II)Ni(II) complexes which differed in the arrangement of the metals at the 4- and 5-coordinate sites. Electrochemical studies showed that Mn(II) and Co(II) ions are stabilised in these complexes and Okawa has attributed this to the "5-coordinate" site adopting a six-coordinate geometry highly distorted from a regular octahedron.

Nagata[177] had synthesised a series of ten dinuclear manganese(II) complexes $[Mn_2(R^1\mathbf{LN6})(\mu\text{-}R^2CO_2)]\cdot ClO_4$ in which both lateral chains of the ligand **LN6** contained methylated N-donors. Substituents on the phenol ring and ligating acetate groups were systematically varied (Fig. 67). He noted that, while other groups[34,48] had reported dinuclear Mn complexes where the Mn ion had two sites for external anions to bind, in his there was only one. His electrochemical studies showed that both the substituents on the phenol ring and the ligating acetate controlled the properties of the Mn(II) centre.



1 : $R^1 = CH_3$, $R^2 = CH_3$
2 : $R^1 = CH_3$, $R^2 = ClCH$
3 : $R^1 = CH_3$, $R^2 = Cl_2C$
4 : $R^1 = CH_3$, $R^2 = CCl_3$
5 : $R^1 = CH_3$, $R^2 = CF_3$
6 : $R^1 = OCH_3$, $R^2 = CH_3$
7 : $R^1 = H$, $R^2 = CH_3$
8 : $R^1 = F$, $R^2 = CH_3$
9 : $R^1 = Br$, $R^2 = CH_3$
10 : $R^1 = Br$, $R^2 = CF_3$

Figure 67

1·5 : Ether containing lateral chains

Kahwa, in his study of molecular recognition events in which hetero- and homo-lanthanide(III) cation pairs were formed, compared the ligand **LO2** formed from the [2 + 2] template condensation of 2,6-diformyl-4-methylphenol and 3,6-dioxaoctane-1,8-diamine to the diaza-containing **LN2** (Section 1·4, p 62). The X-ray structure of the gadolinium complex of $[Gd_2\mathbf{LO2}(NO_3)_4]\cdot H_2O$ (Fig. 68) showed a Gd-Gd pair within the macrocycle, as had been predicted from the magnetic interactions and luminescence studies on both these and the **LN2** macrocycles [37]

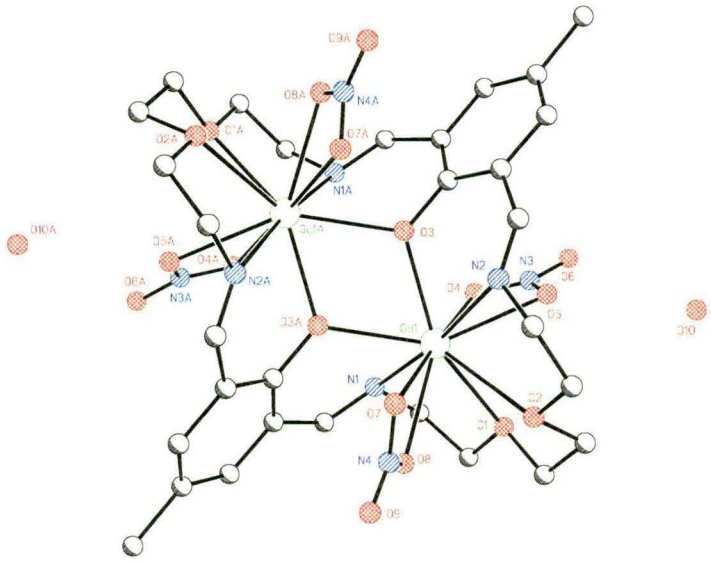


Figure 68

In a continuation of this study Kahwa has made both the reduced and the mixed imine-amine forms of **LO2** and a number of binuclear La complexes of these.[36] The mixed macrocycles appear to be the most stable. It is proposed to add such groups as CH_2COO^- or CH_2CH_2OH to the amine groups in the reduced forms to enhance the ligand binding properties of these complexes.

1·6 : Lateral chains incorporating aromatic moieties

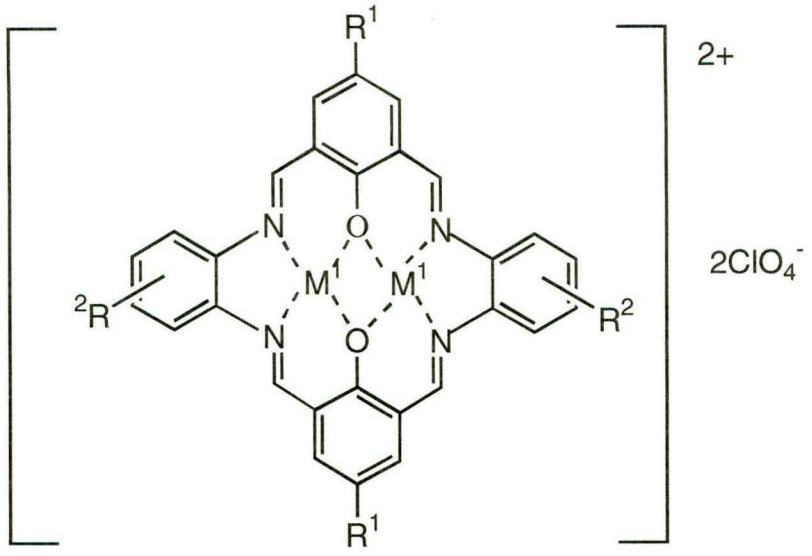


Figure 69 : Complex LDb - Variations are : 1 : R^1 = tBu, R^2 = H, 2 : R^1 = tBu, R^2 = F, 3 : R^1 = $(CF_3)_2CF$, R^2 = F.

The 2,6-bis(aminomethyl)-4-methylphenol ligands of Robson and the diphenyl lateral chains used by Hendrickson[52] have already been discussed. Behrens has formed binuclear copper complexes of **LDb** from 2,6-diformyl 4-t-butyl-phenol and 1,2-diaminobenzene (Fig. 69).[178] These dimerised through an intercalated Mn ion, in a manner analogous to Okawa's CuPb complexes of **L2-2**, to form novel trinuclear complexes (Fig. 70).

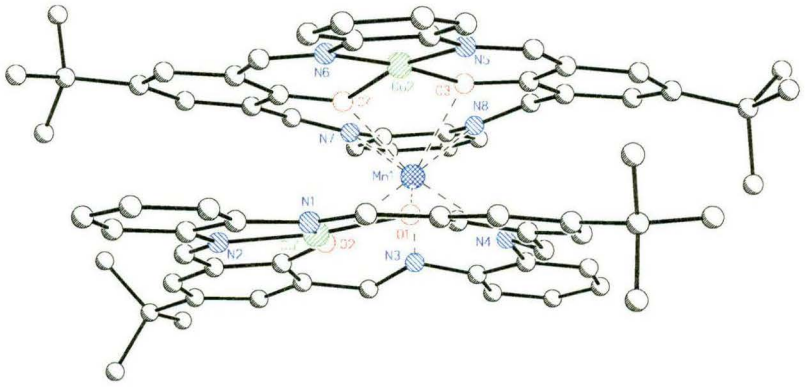


Figure 70 : A representative crystal structure of a complex of LDb

2 : VARIATIONS OF THE PHENOL SUBSTITUENTS

Fine-tuning the reactivity of the metal centres has been the main thrust of the research involving Schiff base macrocycles therefore it would seem that as much interest would have been shown in changing the substituent on the phenol as has been in altering the lateral chains. However, this has not been the case. So far only copper containing podal structures have been synthesised in which the methyl group has been replaced with -OH,[121] $-NO_2$, [119] or -Br.[120] Macrocyclic complexes have been synthesised which contain, in place of the 4-methyl, the $-OCH_3$ group,[177] $-CF_3$,[118] and a number (which are discussed below) with the -Cl substituent.

Kahn[118] compared the CF_3 substituted versions of **L3-3** and **L4-4** to the originals and found that the effect of this substitution was, as expected, to make the dinuclear species more reducible. However this substitution did not modify the magnetic properties of the complexes despite the shift in the reduction wave.

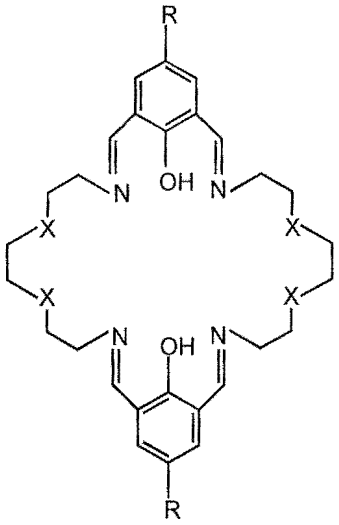


Figure 71 : LO2c , X = O, LN2c , X = N,

Schiff base macrocycles derived from 4-chloro-2,6-diformylphenol and a variety of diamine lateral chains have been used by Vigato's group.[77,179-181] to form binuclear lanthanide complexes. 4-chloro-2,6-diformylphenol used with 1,8-diamino-3,5-dioxaoctane for the formation of H_2**LO2c** (Fig. 71) and a two-step formation reaction with lanthanide nitrates resulted in a series of homo- and

hetero-binuclear complexes of the form $[Ln_2\mathbf{LO2c}(NO_3)_4]\cdot nH_2O$ (Ln = La, Pr, Sm, Eu, Gd, Tb, or Dy; *n* = 1 or 2) and $[Ln_xLn'_{2-x}\mathbf{LO2c}(NO_3)_4]\cdot nH_2O$ (LnLn' = LaSm, LaGd, LaDy, LaEu, DyGd, DyEu, GdEu, GdTb, EuTb, or LaTb; *n* = 1 or 2). The free ligands form almost quantitatively to produce yellow-orange or red solids, stable in air and soluble in common organic solvents, and these were reacted with the metals. Composition of the complexes was determined by elemental analysis and verification of the heterobinuclear nature of the mixed metal species was established by FAB-ms. The presence of a very strong characteristic ν(C=N) IR absorption band centred at 1650 - 1652 cm^{-1} and the absence of ν(C=O) suggests complete closure of these macrocycles.

Table 5 : Experimental and calculated* magnetic moments (295K, B.M.) of the binuclear complexes $[(LnLn'L^1(NO_3)_4]\cdot nH_2O$[181]

LnLn'	*n*	μ_{exptl}	μ_{exptl}^{corr}	μ_{calc}
La_2	1	Diam	Diam	Diam
Pr_2	2	4·59	4·65	4·9
Sm_2	1	1·96	2·10	2·19
Eu_2	1	4·58	4·65	4·9
Gd_2	2	11·28	11·30	11·17
Tb_2	2	13·19	13·20	13·43
Dy_2	1	14·70	14·72	14·78
LaSm	2	1·01	1·34	1·55
LaGd	2	7·68	7·72	7·85
LaDy	1	9·61	9·65	10·45
LaEu	2	3·34	3·45	3·5
DyGd	2	12·67	12·70	13·2
DyEu	1	9·63	9·67	11·02
GdEu	2	7·65	7·70	8·64
GdTb	1	12·41	12·44	12·32
EuTb	2	9·92	9·96	10·12
LaTb	2	9.19	9.22	9.5

* Assuming no magnetic interaction.

The magnetic moments of the heterobinuclear complexes (Table 5) show the absence of metal-metal interaction and appear to indicate the presence of two magnetically dilute lanthanide(III) ions. These results may be explained if the

ligand does not behave as a compartmental* molecule but as a macrocyclic binucleating ligand in which the metal ions are coordinated at a long distance from each other, with no bridging hetero-atom in between them (Fig. 72). This is in contrast to Kahwa's methyl-substituted analogue in which direct metal-metal interaction was observed.[37]

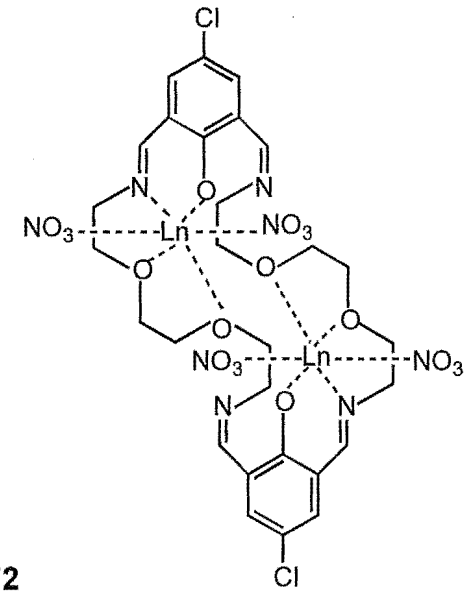


Figure 72

$[H_6\mathbf{LN2c}]\cdot(ClO_4)$ (Z = Cl , $n = m$ = $-(CH_2)_3-N(CH_2-CH_2)_2N-(CH_2)_3-$)[180] was formed while attempting a template reaction with La(III). The X-ray structure of $H_2\mathbf{LPc}$ (Fig. 73) (Z = Cl, $n = m$ = $-C_6H_4-$)[67] showed reduction of two -HC=N- groups to $-CH_2-NH-$ had occurred during the synthetic procedures (this was verified by NMR studies), resulting in the partially reduced Schiff base $H_2\mathbf{LPc}_R$.

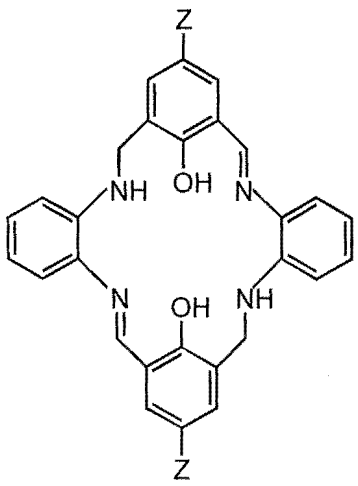


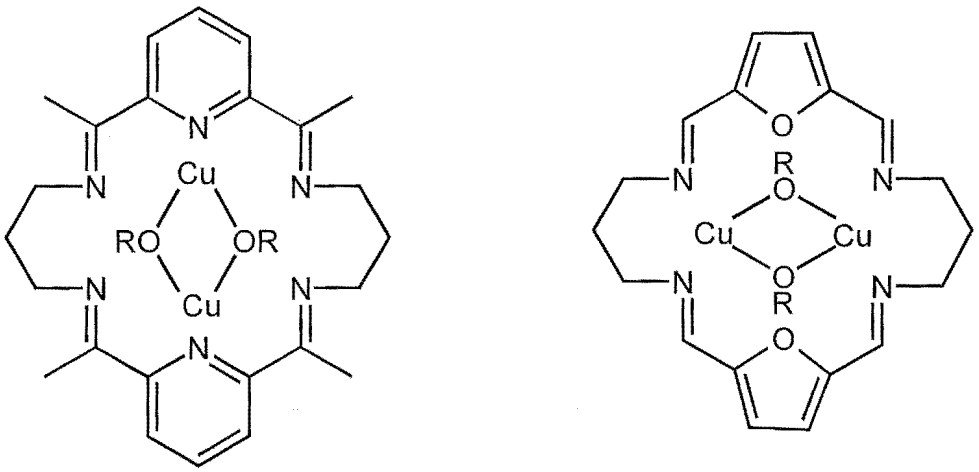
Figure 73 : $H_2\mathbf{LPc}_R$

* Vigato defines a "compartmental ligand" as one in which "two metal centres, if paramagnetic, can interact with each other through bridging groups in a ferromagnetic or antiferromagnetic way"[77]

3 : USES OF THE MACROCYCLES

The importance of both homobinuclear and heterobinuclear and subsequently polynuclear complexes of macrocyclic ligands in many areas of research can not be overstated.[3] As well as being small molecule models for many metallobiosites, they are of interest in the study of ferro- and anti-ferromagnetic exchange coupling, electron transfer properties and the binding and activation of small molecules such as dioxygen. Examples of the use of such complexes to mimic active sites in biological systems have already been given.

3·1 : Host Structures



LP3 **LF3**

Figure 74 : Schematic representation of the copper disposition in pyridine and furan headed macrocycles

Homobinuclear complexes of [2+2] macrocycles have been used as hosts for small bridging ligands.[56,57,181] For example, the copper(II) perchlorate complex of **LP3** (Fig. 74) has been used to prepare several derivatives in which small substrate anions (OH^-, imidazolate, N_3^-, NCS^-) have been bound between the metal centres.[31,182] The crystal structures of the OH^-, imidazolate,[182] and N_3^-,[31] complexes revealed the copper(II) atoms held by the N atoms of the imines and bridged by the anion, with the imidazolate and the N_3^- bridging in the μ-1,3-mode.

Similar dicopper(II) complexes based on a furan ligand head unit also contain μ-hydroxy and μ-alkoxy bridges. The structure of $[Cu_2\mathbf{LF3}(OEt)_2]\cdot(NCS)_2$[183] showed that the copper(II) atoms are bound to the imine N atoms, but not to the furan, leading to a lateral orientation of the copper atoms, rather than head to head as found in the corresponding pyridine complexes (Fig. 74). **LF3** is notable as being the first complex in which thiocyanate bridging through the S-atom only was observed.[184] A series of dicobalt(II) complexes of **LF3** having hydroxo-, alkoxo-, phenoxo-, thiolato-, halogeno-, and pseudohalogeno-bridges has been reported.[185]

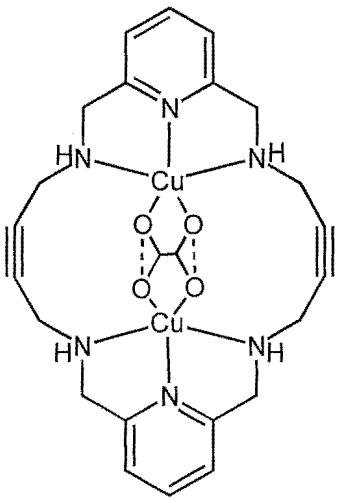


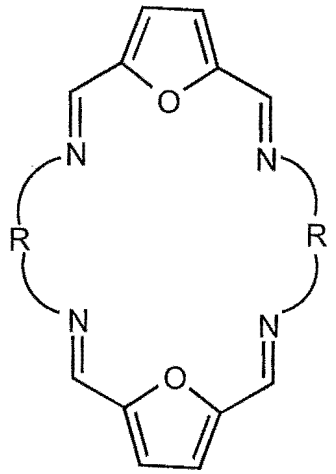
Figure 75

More recently, a bicopper complex resulting from the [2 + 2] condensation of 1,4-diamino-2-butyne with pyridine-2,6-dicarbaldehyde, was shown to be a host structure to an oxalate moiety which bridges two copper ions in a (μ-η^4:η^4) manner.[186] (Fig. 75)

3·2 : Substrate oxidation

The reduction of the copper(II) in both complexes of **LF3** (Fig. 74) has been accompanied by substrate oxidation when PhSH, PhC≡CH, hydrazobenzene, catechols, hydroquinones and ascorbic acid were used giving PhSSPh, PhCtbCC≡CPh, azobenzene, o-quinones, p-quinone and dehydroascorbic acid respectively.[57,183,187] The latter reactions mimic the behaviour of type III copperproteins. When carried out in dimethylformamide solution in the presence of O_2 some of these oxidations by Cu_2**LF3** proved to be catalytic.

The requirement for coordinative unsaturation at the metal centres in the reduced state, was borne out by the inactivity of the $[Cu_2\mathbf{LF3}(OEt)_2]\cdot(NCS)_2$ (Fig. 76) complex. The very poor activity of the mononuclear $Cu(ClO_4)_2$, in the same reaction indicates the requirement for a dicopper site.



R = $-CH_2CH_2CH_2-$

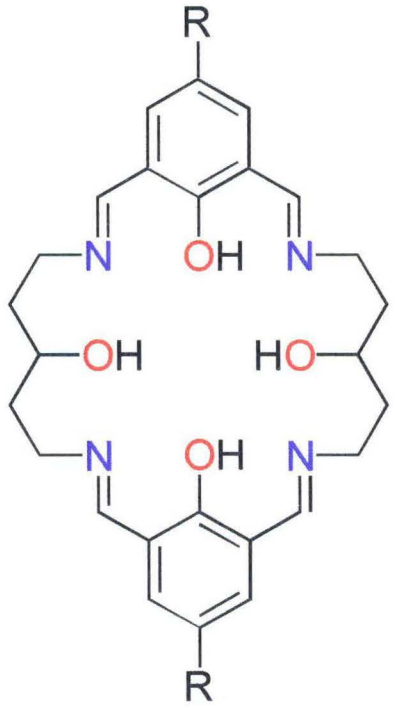
Figure 76

CHAPTER TWO

INTRODUCING THE LV5 AND LV5t LIGANDS

Part one : Setting the scene

1 : INTRODUCTION



H_4**LV5** : R = CH_3, H_4**LV5t** : R = $C(CH_3)_3$

Figure 2·1 : H_4LV5 and H_4LV5t

As mentioned in the review, the macrocycles H_4**LV5** and H_4**LV5t**, (Fig. 2·1) have been prepared by the Schiff-base template condensation of 2,6-diformyl-4-methylphenol or 2,6-diformyl-4-t-butylphenol with 1,5-diaminopentanol and a range of transition metal salts. Each potentially octadentate macrocycle contains four imine donors, two phenol groups and two alcohol groups all of which are capable of bridging metals on deprotonation. Previously these macrocyclic ligands had been used by M^{c}Kee's group to make a series of interesting tetra-[44] and octanuclear copper(II),[45] complexes , a mixed valence manganese complex[47] and tetranuclear Zn(II) and Ni(II) complexes.[157]

interesting tetra-[44] and octanuclear copper(II),[45] complexes , a mixed valence manganese complex[47] and tetranuclear Zn(II) and Ni(II) complexes.[157] These macrocycles have two distinct sections to their construction; the rigid phenol diimine and the saturated side chains which carry the alcohol groups and impart some flexibility to the system. This allows some response to the coordination preferences of the metal ions. The length of the saturated side chain is critical in determining the nuclearity of the final product with tetranuclear products being more readily obtained when 1,5-diaminopentan-3-ol is used. The ligand provides three donors for each ion in a tetranuclear complex and the coordination sphere is completed by exogenous ligands. In many cases, there is also a central oxygen donor binding to all four metal ions. The bridging nature of the ligand donors is the feature of these ligands that enhances the formation of multinuclear complexes.

A feature of H_4**LV5** and H_4**LV5t** is their flexibility. The macrocycle adopts a planar configuration in the tetranickel(II) and tetracopper(II)[44,45,157] complexes but twisted or folded conformations with other metals. As a result the tetranuclear complexes form two distinct groups. The first group comprises copper and nickel. The metal ions show square planar or tetragonal coordination and form planar arrays with open faces. The second group of complexes includes cobalt and manganese. The preference of these metals for 6-coordination results in non-planar bridged complexes. For example, in the mixed-valence $Mn^{II}_2Mn^{III}_2$ complex the metal ions adopt a distorted tetrahedral arrangement about the central oxo ligand. This is in contrast to a similar tetranucleating ligand, reported by Robson,[61] which incorporates four phenolic groups, and adopts a domed configuration with tetranickel(II) and tetrazinc(II) complexes. Mixed-valence redox series are accessible.*

* The research in this project was carried out in two laboratories : at the University of Canterbury (U of C) and the Queen's University, Belfast, N. Ireland (QUB)

2 : AIMS AND OBJECTIVES OF THIS RESEARCH

2·1 : Polymetallic complexes with open planar faces

Modeling bulk properties of metals or metal oxides is of interest in relation to both solid state chemistry and large biological assemblies such as ferritin.[188-189] It has been suggested, from studies in Fe/O/OH systems, that the onset of bulk properties such as superparamagnetism may require as few as 10 - 20 metal atoms. Assemblies of this size straddle the molecular/solid state boundary.[17, 190-192] At present, modeling metal surfaces is a relatively new field of interest.[193] It requires the synthesis of an array of alternating oxygen and metal centres held closely together and containing at least one open face. Although organometallic clusters may contain quite large metal arrays they seldom exhibit vacant coordination sites. Planar macrocyclic ligands such as porphyrins can achieve the required geometry but only for one metal ion. A range of binuclear systems are known.[8,69,108,114,128,150] but only a few ligands have been designed to accommodate larger arrays and these are generally not planar.[14,194,195]

2·2 : This project

There were three distinct areas to be investigated.

Part 1 : The first part was an extension of the work already started on the tetranuclear complexes of the ligands H_4**LV5** and H_4**LV5t** with particular emphasis on making complexes with anions other than acetate. Emphasis was to be placed on complexes of copper, zinc, nickel, manganese and cobalt. Characterisation of these complexes using IR, UV/Vis, chemical analysis, and X-ray crystallography was to be undertaken. It was hoped that as well as tetranuclear complexes of this system binuclear complexes could also be formed and indeed interesting binuclear cobalt complexes were isolated. The binuclear complexes open routes to hetero-tetranuclear complexes of this ligand system. The binding of substrates to the open metal surfaces of the

tetranuclear and octanuclear copper complexes was to be investigated using such techniques as UV/Vis spectroscopy and X-ray crystal structure determination. A number of anions and some organic molecules are used in creating impervious coatings on the surface of metals to protect against corrosion.[196a] Little is known of the chemistry occurring in these processes. The binding of a variety of groups to the central core of the octanuclear complex would model metal surface chemistry and has use in the development of agents for corrosion control.[196b] As this sort of complex was also thought to have potential for catalysis, the complexation of catechol to these macrocycles and its subsequent oxidation, was to be investigated. It is hoped that eventually, the electro-chemistry, electron spin resonance, and magnetic interactions[197] (especially the degree of magnetic frustration) of these complexes will be studied with a view to understanding the metal-metal interactions within them.

The synthesis of a series of tetranickel complexes was to be undertaken. The possible formation of octanuclear nickel complexes, analogous to the copper complexes already made, was to be investigated. The physical properties, catalytic potential and reactivity of the nickel compounds was to be studied in the same way as the copper compounds.

Mixed valence cobalt and manganese systems were to be synthesised. Table 2·1 shows a summary of the complexes already prepared when this project was begun. The asterisks represent the oxidation levels needed to complete the series.

Table 2·1

Co_4^{II}	*	$Co^{II}Co_3^{III}$	*
*	$Mn_2^{II}Mn_2^{III}$	*	*

Part 2 : The second aim of this project was to make an analogue of the H_4**LV5** ligand by replacing the methyl group with a charged substituent. To this end synthesis of 2,6 diformyl-4-sulfonyl phenol (Fig. 2·2) was undertaken. It was proposed that the sulphonated phenol would then be reacted with 1,5-diaminopentanol and the appropriate metal salts. It was hoped that the charged substituent might lead to stacking of the planar complexes and so to compounds capable of catalysis. It was hoped that this interaction would occur from the substituent sulfonate group in one macrocycle to a metal in a neighbouring array, in a manner analogous to the dimerisation of these complexes from the μ-oxo group of one complex to a metal ion of another.

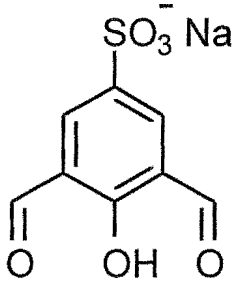


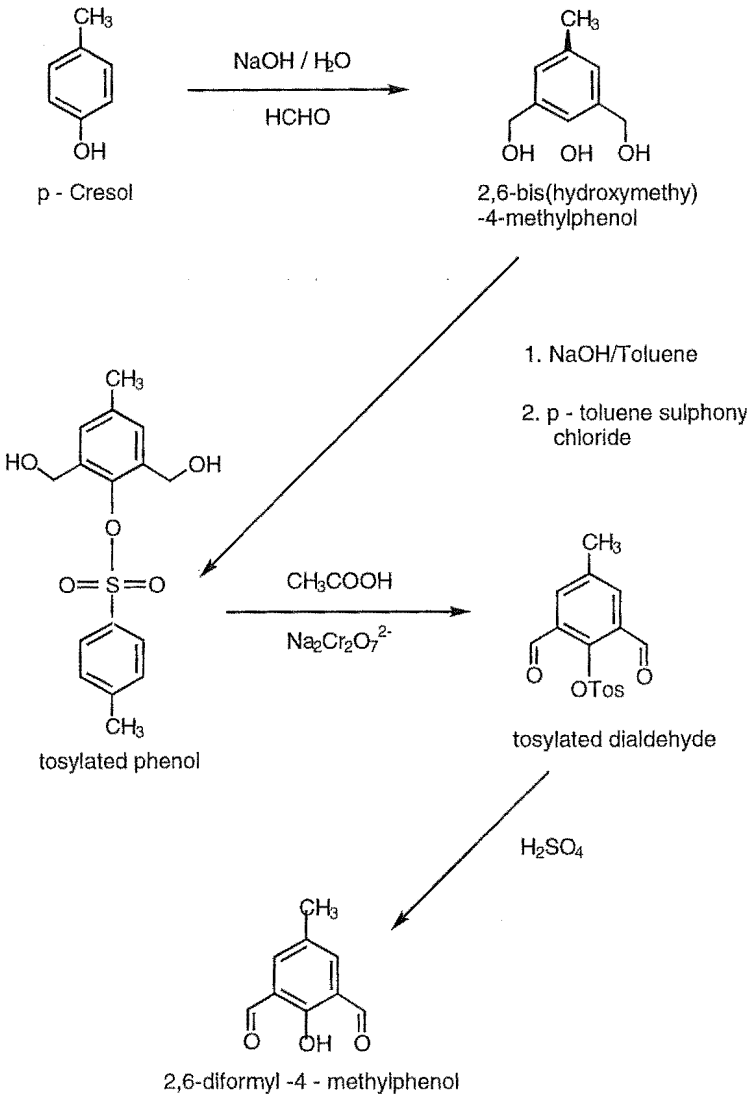
Figure 2·2 : 2,6-diformyl-4-sulphonylphenol sodium salt

Part 3 : The third section of this research was to try and develop a ligand capable of binding six metal centres in a planar array. Although complexes containing more than four metal centres are known (and have been discussed in Chapter 1) few of these are planar. There were two reasons for wanting to develop complexes containing multi-metal centres: firstly planar complexes would be better models for metal surfaces and secondly because of an interest in complexes which straddle the boundary between large complexes and the solid state.

Part Two : General Methods and Syntheses

1 : ORGANIC PREPARATIONS

1·1 : The preparation of 2,6-diformyl-4-methylphenol (dfmp)



Scheme 2·1 : The preparation of 2,6-diformyl-4-methyphenol (dfmp)

At the start of this project the dfmp starting material was prepared (Scheme 2·1) using the method of Gagné *et al.*[35] p-Cresol was treated with sodium hydroxide and formaldehyde to form 2,6-dimethoxy-4-methylphenol. The phenol was protected by the addition of a tosyl group and treated with acetic acid and sodium dichromate to convert the remaining alcohol groups to aldehydes. Finally the tosylated dialdehyde was treated with sulphuric acid, removing the

protecting group, to produce 2,6-diformyl-4-methylphenol. Later in the project, 2,6-dihydroxymethyl -5-methylphenol became commercially available and the first step became unnecessary. New methods[198,199] for oxidising the alcohols were investigated and adopted.

p-Cresol (0·5 mol, 54 g) and NaOH solution (0·625 mol, 25 g in 100 mL H_2O) were mixed. 37% Formaldehyde (1·325 mol, 107·5 g) was added to form a deep orange solution which was stirred 24 h. The 2,6-dihydroxymethyl-5-methylphenol was visible as a thick creamy suspension which rapidly solidified. This was broken up as 100 mL of saturated NaCl was added and was collected by vacuum filtration. This solid was washed with 100 mL and then 50 mL of saturated NaCl.

The total product was transferred to a 3-neck 2 L flask fitted with an overhead stirrer. 325 mL of H_2O and 32·5 mL (0·268 mols) of 33% NaOH solution was added and the mixture stirred for 30 mins. After addition of p-toluenesulfonyl chloride (0·648 mols, 123·5 g dissolved in toluene (180 mL) the mixture was stirred for 20 h. A thick creamy suspension (not aqueous and emulsified phases as suggested in reference 35) was present at this point. 75 mL toluene was added and the mixture stirred 60 min, then a further 25 mL of toluene and 15 mins more stirring. The pale pink tosylated product was collected by vacuum filtration and washed with 2 x 100 mLs of toluene. This product was dried *in vacuo* overnight. Yield : 76·94 g, 0·239 mol, 48%

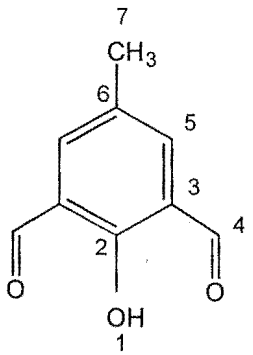
The tosylated phenol (0·239 g, 76·94 g) was transferred to a 3-neck round bottom flask fitted with an overhead stirrer, a reflux condenser and a dropping funnel. Acetic acid (3·346 mol, 200·93 g, 191·54 mLs, i.e. 14 mols per mol of tosylated phenol) and sodium dichromate (1 mol per mol of tosylated phenol) was added. Approximately a quarter of the acetic acid (~ 50 mL) was added to the phenol and brought to reflux with stirring. The dichromate was dissolved in the remaining acid and added dropwise over 75 mins. The reaction mixture was stirred while allowing to cool slowly and left to stand overnight. The product was a deep green viscous suspension. A pale green precipitate was

collected by vacuum filtration and washed repeatedly with water to remove all the Cr^{3+}. A second crop of product appeared in the filtrate over time and was collected and combined with the first. The vacuum dried product was a very pale green powder. Yield : 56·62 g, 0·176 mols, 74 %

The tosylated aldehyde (56·62 g, 0·176 mols) was added to conc. H_2SO_4 (180 mL) in a large beaker and stirred for 1 h. It dissolved to a bright yellow solution which eventually developed a deep brown colour. The beaker was placed in an ice bath and ice water slurry added slowly to the acid solution to a total volume of 750 mL. By this time a creamy coloured fine suspension was visible and when all the ice had melted (after ~ 2 h) this precipitate was collected by vacuum filtration, washed with 50 mL aliquots of water five times and vacuum dried overnight. Yield : 24·09 g, 0·149 mol, 85 %

The dfmp was recrystallised from hot EtOH with the addition of a little water.
Overall yield :15·88 g, 0·098 mol, 16 %
mp : 129 - 135° (Lit. - 133·5°)
Analysis for $C_9H_8O_3$: Calculated :C : 65·84; H : 4·91 %
Found : C : 65·79; H : 5·07 %

IR : ν(C-H) : 3027, 2922, 2870, ν(C=O) : 1682, $\nu(C\text{-}O_{phenol})$: 1216 cm^{-1}.



^{1}H NMR ($CDCl_3$) : H1 : 11·46; H4 : 10·22; H5 : 7·77; H7 : 2.39 ppm.

1·2 : The use of MnO_2 as an oxidising agent

Three methods using MnO_2 to oxidise 2,6-dihydroxy-4-methylphenol to 2,6-diformyl-4-methylphenol were investigated.

In the first, commercially prepared MnO_2 (Jannsen Mn^{IV} precipitated, Cat. no. 20319-46) was heated in an oven at 140°C for 24 hours[199]. The phenol (25g, 0·15 mole) was then refluxed with this MnO_2 (103·38g, 1·19 mole(1 : 8)) in dioxane for 28 h. The reaction mixture was stirred with an overhead stirrer during the refluxing period. The mixture was filtered and the MnO_2 washed with 3 aliquots of MeOH. The filtrate and washings were evaporated to dryness under vacuum. It was obvious that not all of the MnO_2 had been filtered off so the product was redissolved in MeOH and $CHCl_3$ and filtered through HIFLO. The resulting brownish yellow solid was recrystallised from a toluene/MeOH mixture. The yield was 67% but microanalytical data showed that the conversion to aldehyde was not quite total. (Calculated : C : 65·85; H : 4·91; Found : C : 64·09; H : 5·36%).

The second method tried was that of Taniguchi.[198] Again commercial MnO_2 was used. In this method (25g, 0·149 mole) of the phenol was stirred with the MnO_2 (200g, 0·43 moles) at room temperature in $CHCl_3$ (300 mL) for 67 h. This was longer than the recommended 48 h. The resulting mixture was filtered through paper and then through HYFLO Supercell and the golden filtrate reduced under vacuum to produce a pale yellow solid. The yield was 17·61 g (0·107 moles) (after spilling some!) and analysis (Calculated : C : 65·85; H : 4·91; Found : C : 65·53; H : 5·16%) showed it to be more pure than the previous preparation. This method is cleaner and easier to carry out, produces a better yield and a purer product and so became the method of choice.

The third investigation was to test a method of making MnO_2 as the commercial product is quite expensive. MnO_2 was made by roasting $MnCO_3$ at 250°C for 5 h. This was used in Taniguchi's method and the yield was poorer and the product not as pure as that for the other two methods. A better method for the preparation of MnO_2 is that of Papadopoulos[200] in which $MnSO_4$ in boiling water is treated with $KMnO_4$ and the resulting MnO_2 filtered off and dried.

From a literature search it would seem that the use of $BaMnO_4$ as an oxidising agent may be even better than MnO_2.[201] One of the advantages of $BaMnO_4$ is

that it does not deactivate once made. Future work will include making and investigating this oxidising agent.

1·3 : The preparation of 2,6-diformyl 4-t-butylphenol

Preparation of 2,6-diformyl-4-*t*-butylphenol was by the method of Drago *et. al.*[202] who modified the four-step procedure of Ullman and Brittner.[203] 4-*t*-Butylphenol was converted to 2,6-methoxy-5-*t*-butylphenol in an alkaline formaldehyde solution. The phenol was then protected with a tosyl group and the alcohol groups oxidised to aldehydes. Finally the protecting group was removed.

4-*t*-Butylphenol (150 g, 1 mol) was added to NaOH (50 g, 0·8 mol) in 1·2 L of water, and the mixture stirred with heating to dissolve the phenol. A brown solution formed. The mixture was cooled to room temperature, formaldehyde solution (37 %, 157 mL, 2·1 mol) was added and the mixture stirred at room temperature for ~ 120 h. Upon addition of 110 mL of concentrated HCl, an aqueous phase with suspended NaCl and a yellow organic phase formed. The organic phase was isolated and washed with three 50 mL aliquots of water. $CHCl_3$ (700 mL) was then added with another 500 mL of water. The mixture was stirred and the two phases allowed to separate. The organic phase was isolated and dried with 100 g of anhydrous $MgSO_4$. This chloroform solution was filtered, reduced under vacuum to a deep brown oil and left in the cold room overnight. The product was a brown oil containing large clear crystals. 75 mL of $CHCl_3$ was added and a white precipitate appeared immediately. More $CHCl_3$ was added until the product resembled light brown fudge at which point the white solid was collected under vacuum and washed with a little $CHCl_3$. The solid was dried *in vacuo*. Yield : 140·0 g, 0·7 mol, 70 %

2,6-Dimethoxy-4-*t*-butylphenol (140 g, 0·7 mol) was added to 500 mL of water and NaOH (34·04 g) in a 5 L round-bottom flask fitted with an overhead stirrer. Toluenesulfonyl chloride (133·2 g) was added with 150 mL of benzene and the yellow suspension stirred vigorously for two days. The mixture was filtered

under vacuum to yield a white solid which was then washed with 3 x 150 mL of benzene. The tosylated phenol was air dried. Yield : 118 g, 0·39 mol, 58 %

The tosylated diol (118 g, 0·39 mol) was dissolved in 500 mL of glacial acetic acid, in a large beaker, with heating and stirring. When the solution was almost at boiling point 100 g of $Na_2Cr_2O_7 \cdot H_2O$ was added very slowly to ensure that the mixture did not boil over. A white powdery solid formed in the deep green solution. The mixture was allowed to cool slowly to RT and left to sit overnight. The product was collected from the chromium salt solution by vacuum filtration and washed with water twice and a water - ethanol (3 : 1) mixture once. The solid was dissolved in 800 mL of boiling EtOH and 80 mL of water was added. The mixture was allowed to cool while stirring and then allowed to sit for 4 days after which time a white crystalline product (40 g) was filtered off. The filtrate was allowed to stand and after a period of time a further 10 g of product was collected. Yield : 50 g, 0·145 mol, 37 %.

The tosylated diformyl product (50 g) was added to 70 mL of concentrated H_2SO_4. The solution was stirred for an hour and then poured cautiously into 1·5 L of ice slurry in a 3 L beaker. The ice-water mixture was stirred for 3 h and the brown solid collected by vacuum filtration. The solid was dissolved in hot MeOH and water added until turbidity was obvious at which point the mixture was reheated until it became clear. Slow evaporation yielded a semicrystalline brown product. Yield : 25 g, 0·121 mol, 84 %

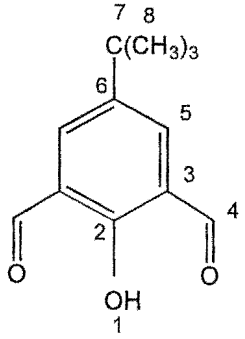
Overall yield 12 % based on *t*-butylphenol (Lit. 10 - 20 %)

This product has been prepared in 27 % yield[204a] using Taniguchi's[198] method of oxidising the dialcohol.

MP : 101 - 103°C (Lit. 105°C)

Analysis for : $C_{12}H_{14}O_3$

Calculated :	C : 69·86;	H : 6·84 %
Found :	C : 70·12;	H : 6·64 %



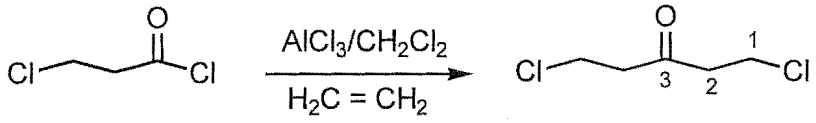
NMR ($CDCl_3$) : ^1H : H1 :11·5; H4 : 10·3; H5 : 8·0; H8 : 1·4 ppm.

^{13}C : 31·0; 34·2; 122·6; 134·6; 143·0; 161·6; 192·5 ppm.

1·4 : Preparation of 1,5-diaminopentan-3-ol dihydrochloride

1,5-Diaminopentan-3-ol was prepared in 68% overall yield from 3-chloropropionyl chloride in four steps (as discussed below) by adapting the overall method of Owen *et al*[205] and Murase *et al*[206]. This was an improvement over the previous 16% reported by Brooker.[207]

Step 1 : 3-chloropropionyl chloride → 1,5-dichloropentan-3-one



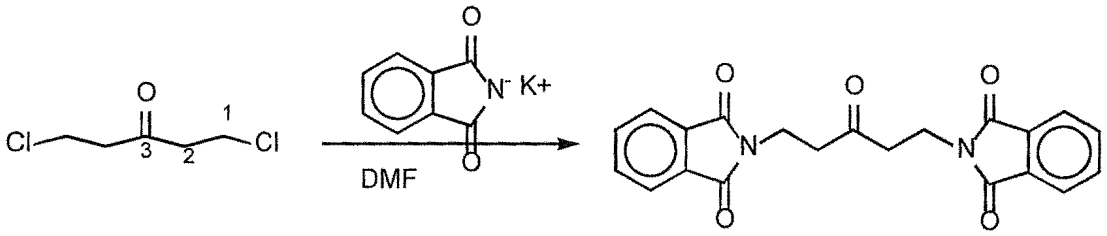
The Friedel-Crafts alkylation as reported by Owen was carried out. 3-Chloro-proprionyl chloride (100g, 0·76 mol) was added slowly to a mechanically stirred and cooled (ice bath) suspension of dry $AlCl_3$ (147g, 1·10 mol) in dichloro-methane (200 mL - dried over sieves). The reaction was carried out in a three-necked flask. HCl gas was evolved during the addition. The solution was allowed to warm to ambient temperature and ethylene gas was added to the mixture for a minimum of 5 hours. It was found that really vigorous stirring at this step of the reaction significantly increased the yield and that it was not necessary to have the gas bubbling through the mixture but simply replacing the ethylene atmosphere as it was used, was sufficient. The golden solution was then tested for starting material by taking about 0·1 mL, adding the same amount of water, separating the CH_2Cl_2 layer, and after evaporating the

CH_2Cl_2, examining the infrared spectrum of the remaining oil. An absorption at 1715 cm^{-1} was indicative of the product and the disappearance of the initial carbonyl band at 1790 cm^{-1} verified the completion of the reaction. The yield was further increased by continuing to stir the stoppered reaction for some time, e.g. overnight, after the gas flow had been discontinued. The resulting solution was then added cautiously, maintaining the temperature below 20°C, to a slush of ice (400mL i.e. the aqueous layer), dichloromethane (100mL) and conc. HCl (40mL) in a high sided beaker. A little extra HCl was added to ensure that all the $AlCl_3$ had been removed. The blue-black organic phase was separated, washed with 4 x 400mL of water, the water layers were saved and re-extracted with CH_2Cl_2 and the combined organic layers dried over $MgSO_4$ for two hours. Evaporation of the dichloromethane under vacuum left 1,5-dichloropentan-3-one as a blue-black oil (114 g, 0·717 mol, 94 %) The greatly improved yield (94 % *cf* Lit. 55 %) is partly attributed to the vigorous and prolonged mixing with the ethylene at this step of the reaction.

IR : ν(C-H): 2972, ν(C=O): 1720 cm^{-1}

NMR ($CDCl_3$) : ^1H : H1 : 2·94(t), H2 : 3·76(t) ppm

Step 2 : 1,5-dichloropentan-3-one → 1,5-diphthalimidopentan-3-one



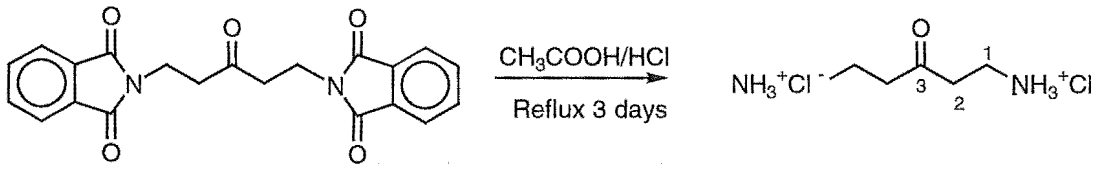
Phthalimide groups were substituted for the chlorides by the method of Murase *et al.* It was decided that the phthalimide should be in at least a 2 : 1 ratio to the ketone at this step (for some reason none of the previously reported syntheses have greater than a 1·3 : 1 ratio). Potassium phthalimide (329 g, 1·772 mol) was vigorously stirred in dimethylformamide (630 mL, dried over molecular sieves), while crude 1,5-dichloropentan-3-one (140·96 g, 0·886 mol) was added dropwise over one hour during which time the suspension increased in temperature and changed colour from white to brown. The resulting mixture

was heated at 80-85°C for 6 h and allowed to stand at room temperature overnight. The resulting 1,5-diphthalimidopentan-3-one was collected in a frit under vacuum and washed successively with chloroform (as this wash removes the excess organics it was repeated), water and acetone to produce a white powder. Yield : 191·66 g, 0·509 mol, 66·5 %.

IR : 1774(s), 1708(s,b)

NMR (DMF) : ^{13}C : C1 : 33·37; C2 : 40·87; C3 : 206·92; C4 :168·50;
C5 : 132·73; C6 : 123·55; C7 : 134·97 ppm

Step 3 : 1,5-diphthalimidopentan-3-one → 1,5-aminopentan-3-one dihydrochloride

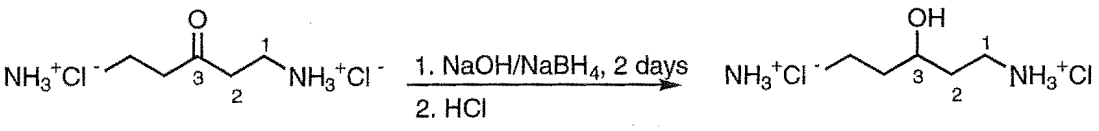


The harsh reaction conditions outlined by Murase *et al* were used to cleave the five-membered phthalimide ring releasing phthalic acid (a by product) and 1,5-diaminopentan-3-one dihydrochloride. 1,5-Diaphthalimidopentan-3-one (189·87 g, 0·509 mol) was boiled in a mixture of acetic acid (475 mL) and conc. HCl (306 mL) with additional 17 mL aliquots of conc. HCl being added at 8 hourly intervals over a period of 3 days until 170 mL had been added. On cooling, the fawn precipitate of phthalic acid was filtered off and washed with water. The combined filtrates and washings were evaporated nearly to dryness under reduced pressure, ~ 400 mL of water added and the undissolved phthalic acid filtered off. The filtrate was concentrated to ~50 mL under vacuum, ~700 mL of ethanol added and the resulting white precipitate, 1,5-diaminopentan-3-one dihydrochloride collected in a frit under vacuum. If pure ketone is required it is best to rinse the product with EtOH as the phthallic acid is soluble in this but the ketone is not. Yield : 93·17 g, 0·493 mol, 96·8 %.

IR : 2997(sb), 1716(s), 1581(s), 1520(s) cm^{-1}

NMR spectra (D_2O) ^1H : H1 : 3·14(t); H2 : 2·91(t) ppm
^{13}C : C1 : 39·33: C2 : 34·75: C3 : 209·10 ppm

Step 4 : 1,5-diaminopentan-3-one dihydrochloride → 1,5-aminopentan-3-ol dihydrochloride



Reduction of the carbonyl function to an alcohol was carried out by the method of Murase *et al.* Several aliquots of 1,5-diaminopentan-3-one dihydrochloride (37·01 g, 0·196 mol total) were added to a solution, maintained below 20°C, of NaOH (15·6 g, 0·39 mol) and sodium borohydride (10·97 g, 0·29 mol) in 300mL of water. The reaction solution was stirred at room temperature for 48 h after which time 2M HCl was added slowly and carefully to the cold solution until the pH was ~1. The solution appeared black during this step but reverted to colourless on standing. The solution was evaporated under vacuum to a dry white solid. Excess boric acid was removed, as its methyl ester, by adding methanol to this product and then evaporating off the ester under vacuum. The addition of methanol and evaporation to dryness were repeated three times. 100 mL of methanol were added to the final residue, the mixture refluxed 30 minutes, cooled and filtered to remove the resulting NaCl. The final step is to concentrate the filtrate and pour it into diethylether. This usually resulted in a lump of product which then had to be recrystallised to purify it. It was decided to try adding the oil product to stirring diethylether to prevent it settling into a lump. The filtered solution was concentrated to ~ 90 mL and then added slowly to 900 mL of stirring diethylether. This was most easily achieved by allowing the oil to drip slowly through a filter paper into the ether. A white powdery product formed immediately on contact of the oil with the ether and more product formed if the mixture was allowed to sit in the refrigerator at ~ 4°C overnight. This method achieved an almost quantitative conversion at this step and the melting point and chemical analysis showed that the product was pure enough not to require recrystallisation. This adaptation is considered to be the second factor in the greatly improved overall yield of this preparation.
Yield : 39·48 g, 0·206 mol, 105 % (wet).

m.p. : 156·8 - 158°C for the crude product (Lit. : 158-160°C recryst. from MeOH - Ether).

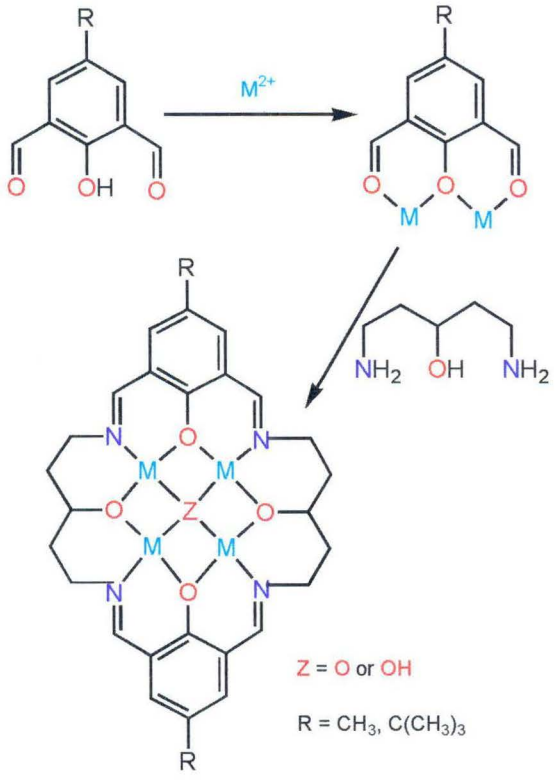
Infrared spectrum *inter alia* 3380(sb), 3030(sb) , 1600(s), 1570(s) cm^{-1}

NMR (CD_3OD) : ^1H : H1A, H1B : 3·09(m); H2A, H2B : 1·84(m); H3 : 3·86(m) ppm

^{13}C : C1 : 68·58; C2 : 335·66; C3 : 38·60 ppm

Overall Yield : 68 % (Lit. 16 %).

2 : PREPARATION OF THE MACROCYCLES



Scheme 2·2 : Proposed Formation of the Macrocyclic Complexes

Essentially all of the complexes were synthesised by the same template procedure and only variations of this will be recorded in detail. The reaction is thought to proceed by the mechanism shown in Scheme 2·2; 2,6-diformyl-4-methylphenol or its derivatives react with a metal(II) salt[208] to form a dinuclear complex. Such a species is expected to readily form a symmetrical [2+2] Schiff-base macrocycle upon condensation with a diamine, the components having assembled around the template metal ions in the appropriate arrangement for this formation.

The appropriate metal salt (4 mmol) was refluxed and stirred with 2,6-diformyl-4-methylphenol (2 mmol, 0·324 g) or 2,6-diformyl 4-t-butylphenol (2 mmol, 0·408 g) in hot dry ethanol, methanol or a mixture of both for ~ 10 minutes. A solution of 1,5-diaminopentan-3-ol (dahp) (2 mmol) was added dropwise to the refluxing metal-salt and phenol and the resulting mixture refluxed with stirring. At the beginning of the project a solution of 1,5-diaminopentan-3-ol (dahp) was made from the dihydrochloride salt (2 mmol, 0·382 g) by neutralising the salt with KOH (4 mmol, 0·224 g) in ~ 20 mL of dry 1 : 1 MeOH : EtOH. This usually took a long time (> two hours) to dissolve and it was difficult to decide if the reactants were dissolved or if the visible solid was the resulting KCl appearing. For this reason, in later experiments, it was decided to dissolve the dahp and KOH separately, with heating and stirring, in the minimum of dry solvent. These two solutions were then mixed and the resulting mixture stood in ice for 60 or more minutes to precipitate the maximum amount of KCl. Eventually, this method was further refined by prepreparing a bulk 500 mL solution of KOH at 0·399 mol L^{-1}. A 10 mL aliquot contained 4 mmols and was used to release the diamine from the dissolved dihydrochloride salt. The 1,5-diaminopentan-3-ol solution was then added dropwise to the refluxing metal-salt and phenol mixture by allowing the solution to drip slowly through a filter paper in a funnel sitting in the top of the condenser and rinsing this with MeOH.

Initially, the reaction mixtures were refluxed twenty-four hours but later in the study it was found that the yields in some of the reactions (notably the cobalt syntheses) were enhanced if the refluxing was for longer. Because of this many of the syntheses were repeated with much longer reaction times. The products either appeared in the reaction mixture as crystalline or very finely divided solids and were collected under vacuum from the hot reaction mixture, or were recovered after cooling and concentration of the mixture. In some instances, the product appeared after as little as 6 h. There were varying degrees of success with this preparation depending on the metal involved. The best yields were for the copper complexes. The nickel complexes, because they are the most soluble, were the most difficult to collect. Even using the procedures described above it was not possible to completely exclude the KCl

from these reactions and the presence of the chloride ions led to the recovery of new complexes which will be described later.

The practical part of this study was carried out in two locations - The University of Canterbury, Christchurch, New Zealand and The Queen's University, Belfast, Northern Ireland. Many of the reactions first tried in one place produced different products when repeated in the other. For this reason, for the sake of reproducibility, many of the preparations were repeated a number of times. The formation of different products, from essentially the same reaction, is interesting in itself and attempting to find explanations for this is one of the on-going parts of this study.

3 : METAL SALTS

Metal perchlorates : The metal perchlorate salts were prepared by mixing the appropriate metal carbonate with perchloric acid (70 %). The resulting slurries were concentrated by gently heating over a water bath and then allowing to cool and crystallise. The resulting crystals were collected by vacuum filtration and recrystallised twice from water. The crystalline products were dried under vacuum overnight.* The salts were stored in a desiccator

$Fe(II)(ClO_4)_2$ was prepared by stirring electrolytic grade iron powder in dilute perchloric acid (~3 : 1 acid : H_2O) **without** heating. More powder was added while gas continued to be evolved, but the solution was filtered while it was still acidic. It is necessary to test for this constantly as if all the acid is used the iron oxidises. The solution was treated as for other metal perchlorates. The solution started out a yellowy-red colour (very pale) and usually becomes pale green. This solution went bright yellow but on filtering the product was green.

Cobalt thiocyanate was prepared by M^{c}Kee using the method reported by Schlessinger.[209b] In this method lead nitrate is reacted with potassium or sodium thiocyanate to form lead thiocyanate. The lead thiocyanate is then

* Great care was taken in the preparation of perchlorates. Mixtures were heated over steam baths and heating and vacuum drying was done behind the appropriate safety shields.

stirred with boiling cobalt sulfate and after the resulting lead sulfate is precipitated the mixture is filtered and the remaining cobalt thiocyanate extracted as a fine brown powder.

4 : SOLVENTS AND ORGANIC REAGENTS

Solvents for preparative chemistry were chemically pure grade and were used without further purification unless stated otherwise. Chemicals which were not prepared in this work were analar or reagent grade and were used without further purification.

Methanol and **ethanol** were dried by first placing the solvents over dried molecular sieves. The solvents were then dried by a process which involved the formation of magnesium methylate or ethylate and the subsequent removal of the water in the manner shown in the following equations.[210]

$$Mg + 2CH_3CH_2OH \rightarrow H_2 + Mg(OC_2H_5)_2$$

$$Mg(OC_2H_5)_2 + 2H_2O \rightarrow Mg(OH)_2 + 2CH_3CH_2OH$$

To dry 1 L of solvent clean dry magnesium turnings (5 g) and iodine (0·5 g) were placed in a 2 L round bottom flask fitted with a condenser and drying tube. EtOH (50 - 75 mL dried over sieves) was added and the mixture heated in a heating mantle until all the I_2 had disappeared and the ethoxide (a white precipitate) had formed. The remaining EtOH (900 mL) was added and the mixture refluxed for at least 3 h. The dried solvent was distilled off into the vessel in which it was stored.

Acetonitrile was dried by shaking with molecular sieves, stirring with CaH_2 until no further hydrogen was evolved (this leaves only traces of water and removes acetic acid) and finally distilling over 0·5 - 1·0 % (weight per volume) P_2O_5.

Tetraethylammonium perchlorate (TEAP) was prepared for use as an electrolyte in cyclic voltammetry. 150 mL (~25 %) tetraethylammonium hydroxide were mixed with 150 mL of concentrated perchloric acid in a 1 L conical flask standing in an ice bath. The solution was diluted with H_2O in 150 mL aliquots. At the second addition a white crystalline solid appeared and after the third addition the mixture was left to stand in the ice bath. The masses of fine colourless crystals that appeared were collected in a sintered glass funnel and redissolved in an EtOH : H_2O mixture with gentle heating. This solution was allowed to stand (in a fumes hood) until a good crop of colourless crystals formed. This TEAP was collected by vacuum filtration, transferred to a round bottom flask which was attached to a vacuum line and heated in an oil bath at 45 - 65°C. The TEAP was dried in this manner for a total of 11 h.
Yield : 72·72 g, 0·317 mol, 78·67 % (based on 150 mL of perchloric acid being 0·403 mol).

Tetraethylammonium chloride was made be heating equimolar amounts of tetraethylammonium hydroxide with concentrated hydrochloric acid in an evaporating dish on a steam bath. The mixture was heated until all liquid was driven off and the resulting solid caked material was dissolved in hot EtOH and the solution transferred to a beaker. On cooling ether was added and the product allowed to precipitate out. The product was collected by vacuum filtration and more ether added to the filtrate to cause a second precipitate.

5 : INFRARED STUDIES

Infrared (IR) spectroscopy is the first method of identification of the products of these reactions. The infrared spectra[211] of all the complexes are broadly similar, except for those vibrations associated with the anions. The macrocyclic nature of the complexes is confirmed by the disappearance of the carbonyl (1688-1660 cm^{-1}) and amine (3300-3200 cm^{-1}) stretches of the reactants and their replacement by strong vibrations, due to υ(C = N), at 1625–1655 cm^{-1} which indicate that the cyclisation has taken place.

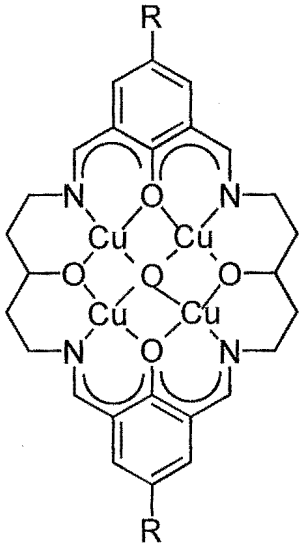


Figure 2·3

Strong bands at 1535 - 1550 cm $^{-1}$ are attributed to υ (C ---- O) and υ (C ---- C) of the phenols.[43] A band at 1550–1580 cm^{-1} is assigned to the C–O vibration of the phenol. The phenol C–O vibration in the complexes absorbs at a higher frequency than the normal alcohol C-O frequency (1200-1000 cm^{-1})* due to the conjugation in the chelate ring which results in the phenol C–O bond attaining a partial double-bond character (Fig. 2·3).

An envelope of weak to strong intensity[114] in the region of ~ 3450 cm $^{-1}$ observed in the spectra of all the compounds (recorded as KBr discs) is due to the O–H stretches of the H_2O in the samples or in the KBr discs used. Usually no sharp O–H stretches could be distinguished.

6 : MASS SPECTROMETRY

Mass spectrometry has been used extensively in elucidating the structures of the macrocyclic complexes. It has been particularly important where it has been difficult to decide if the metal ions are incorporated within the macrocycle or are part of a complex anion e. g. $CoCl_4^{2-}$. This ion and other metal complexes, such as $Co(H_2O)_4(CH_3CN)_2$, have been found and verified by X-ray crystallography, amongst the complexes synthesised. Although elemental

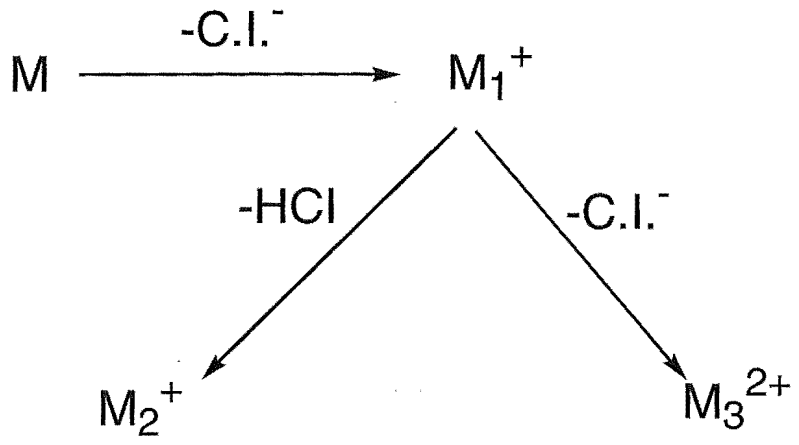
* The phenol C-O band of 2,6-diformyl-4-methylphenol appears at 1216 cm^{-1} and that of 4-*t*-butyl-2,6-diformylphenol at 1220 cm^{-1}.

analysis results could be interpreted as showing that a structure contained four metals it required analysis of the mass spectrum to show if these were incorporated within the macrocycle.

Fast atom bombardment mass spectrometry (FAB-ms) was the method most often used but electron impact mass spectrometry (EI-ms) was also used. In FAB the surface layer of the sample is a mixture of matrix and substrate. Ion intensity is dependent on the activity and solubility of the sample in the matrix as well as the concentration of the sample in the matrix. This means that sometimes very little sample signal is seen above the matrix signal. Each time the sample is bombarded a new surface layer is exposed. The most intense region of the beam is 3 - 4 mm in width and within this area the sample-matrix mixture is reasonably quickly ablated. This is the reason that the sample cannot be applied to the target without the use of any matrix at all - it would simply disappear too quickly. The fact that the sample is dried on the probe can lead to loss of sensitivity if the surface layer containing most of the sample is lost in the drying process.

For the compounds isolated in this study, it is not uncommon to find an ion that is three mass units lower than that expected for the macrocycle and four incorporated metals. The overall charge on the macrocycle is 4^- and if it contains four metals in the 2^+ oxidation state the overall charge of the complex is 4^+. Ions are detected on a mass to charge ratio and it appears that, within the mass spectrometer, the complex will lose three hydrogen ions to give an M^+ ion. Counterions leaving the complex can go as an ion (e.g. Cl^-) or as the neutral species (e.g. HCl) (Fig. 2.4).

The relative percentage of ions, for all spectra reported in this thesis, are those obtained after subtraction of the matrix ions.



C.I. = Counterion

Figure 2·4 : The loss of fragments during Mass Spectrometry

7 : PHYSICAL MEASUREMENTS

Infrared spectra were recorded from 450 cm^{-1} to 4000 cm^{-1} on Perkin Elmer 1600 Fourier-transform infrared spectrophotometer as KBr pellets or as nujol mull. Spectra for selected complexes are given in Appendix I. Elemental analysis was carried out in New Zealand by the Microanalytical Laboratory, University of Otago, Dunedin; in Belfast on a Perkin-Elmer PE240 automatic CHN analyser by ASEP (QUB). Magnetic susceptibility measurements and electron paramagnetic resonance spectra were obtained through the courtesy of Dr. C. J. Harding from the Open University, Milton Keynes, U.K. NMR spectra were obtained using Varian Unity 300 spectrometer, at the operating frequencies of 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR). Fast-atom bombardment mass spectra (FAB-ms) were obtained using Kratos MS80 RFA mass spectrometer operating at 4 kV, with FAB gun 2N11NF (IonTech) and Xe gas at 8 kV. Electron impact mass spectra (EI-ms) were obtained on the same instrument. Selected spectra are given in Appendix II.

8 : CRYSTALLOGRAPHY

X-ray crystallographic data were collected on either a Nicolet R3m (U. of C.) or a Nicolet P4 (QUB) four-circle diffractometer using graphite-monochromated Mo-K_{α} radiation (λ = 0·71073 Å). The unit cell parameters were determined by the least-squares refinement of 12 to 25 accurately centred reflections in the

range $8 < 2\theta < 25$ °. Crystals suitable for X-ray crystallography were mounted on a glass fibre using a hydrocarbon oil and transferred into the nitrogen stream of the diffractometer. Most data sets were collected at a temperature of ~ -130 K. The crystal stability was monitored by recording three check reflections every 97 reflections and no significant variations were recorded for any of the data sets. The data sets were corrected for Lorentz and polarisation effects, and unless other wise stated, an empirical absorption correction was applied, based on φ-scan data. Heavy atom positions were determined by direct methods. Hydrogen atoms were inserted at calculated positions using a riding model with thermal parameters equal to 1·2U of their carrier atoms. Neutral scattering factors were taken from Ibers and Hamilton.[212] Structures **2**, **79**, **132,** and **134**, were refined on F^2 using full-matrix least-squares refinement; the function minimised in the refinement being $\Sigma[w(F_o^2 - F_c^2)^2]$ where $w = [\sigma^2(F_o)^2 + (aP)^2 + bP]^{-1}$ and $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$. These structures were solved using the programme SHELXS-86[213a] and refined using SHELXL-92[213b] or SHELXL-93.[213c] The rest of the structures were refined on F using the programme SHELXTL[213d] version 4·2; the function minimised in the refinement is $[\Sigma(w \cdot |F_o - F_c|^2)]^{1/2}$, where $w = [\sigma^2(F) + |g| \cdot F^2]^{-1}$. Structures **33**, **133**, and **138** were further refined using SHELXL-96. Final atom coordinates and numbering schemes are given in Appendix A, and tables of selected interatomic distances are given in the appropriate parts of the discussion.

Note - numbering of the complexes reported in this work.

The complexes referred to in Chapter One have been coded in a manner which has been explained in the text. This same code will be used wherever these complexes are referred to in this work. Complexes synthesised in this project and reported here will be numbered sequentially. All other complexes referred to will have the prefix **M** and be numbered sequentially.

CHAPTER 3

THE COPPER COMPLEXES

1 : INTRODUCTION

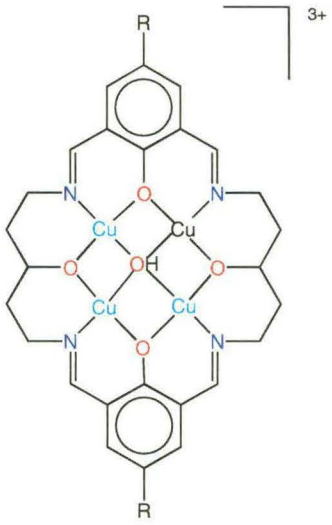


Figure 3·1 : Tetranuclear Copper complex of LV5 (R = Me) of LV5t (R = tBu)

The following copper complexes of the **LV5** ligand system (Fig 3·1) had previously been reported by M^{c}Kee[43]. The stoichiometries of the complexes were initially assigned on the basis of analytical data and were confirmed by spectroscopic studies and, for complexes **M3, M7, M9** and **M10**, single crystal X-ray structure determinations.

M1 $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(NO_3)_3]\cdot 2H_2O$

M2 $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]$

M3 $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5t}(NO_3)_3]\cdot H_2O$

M4 $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5t}(ClO_4)_3]\cdot 2H_2O$

M5 $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(CH_3COO)_3]\cdot 3H_2O$

M7 $[\{Cu_4(\mu_5\text{-}O)\mathbf{LV5}(ClO_4)\}_2]\cdot 3dmf$

M8 $[\{Cu_4(\mu_5\text{-}O)\mathbf{LV5t}(NO_3)\}_2]\cdot(NO_3)_2\cdot 2H_2O$

M9 $[\{Cu_4(\mu_5\text{-}O)\mathbf{LV5t}(ClO_4)\}_2]\cdot(ClO_4)_2$

M10 $[Cu_4(\mu\text{-}N_3)_2\mathbf{LV5t}(N_3)_2]\cdot 2CH_3OH$

The seven new complexes discussed here have been identified by IR, chemical analyses and mass spectrometry as three tetranuclear (**1**, **2**, **4**), one binuclear (**3**) and two octanuclear complexes (**5, 6**,) of **LV5**. Complex **7** is a tetranuclear complex of a variation ligand of **LV5**. Crystal structures for **2**, **5**, and **7** are also discussed.

1 $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot 4H_2O$

2 $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(CH_3CN)_3(ClO_4)_2]\cdot ClO_4\cdot H_2O$

3 $[Cu_2(H_2\mathbf{LV5}(ClO_4)_3Cl]\cdot 2H_2O$

4 $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot CH_3CH_2OH$

5 $[\{Cu_4(\mu_5\text{-}O)\mathbf{LV5}(ClO_4)\}_2]\cdot(ClO_4)_2\cdot 4H_2O$

6 $[\{Cu_4(\mu_5\text{-}O)\mathbf{LV5}(ClO_4)\}_2]\cdot(ClO_4)_2$

7 $[Cu_4(H_2\mathbf{LV5})(dfmp)_2Cl(H_2O)_2]$

2 : SYNTHESIS AND IR OF THESE COMPLEXES

All of the copper complexes made with the **LV5** system, with the exception of complex **7**, contained the perchlorate anion. Complex **7** contains BF_4^-. The reaction mixtures of dfmp (2mmol), dahp (2 mmol) and the appropriate copper(II) salt (4 mmol), were refluxed for ~24 h and all the copper complexes were obtained as forest green to very deep green powders. The first yields varied from 39 to 82 %. Crystals for **2** and **6** came from recrystallisation of the powders but **7** was collected after slow evaporation of the filtered reaction mixture.

Features found, regardless of the metal or anion used, in all the compounds made with this ligand system are the disappearance of the carbonyl (1688-1660 cm^{-1}) and amine (3300-3200 cm^{-1}) stretches of the reactants and their replacement by strong vibrations, due to υ(C = N), at 1625–1655 cm^{-1} which indicate that the cyclisation has taken place. Strong bands at 1535 - 1550 cm^{-1} are attributed to υ (C ---- O) and υ (C ---- C) of the phenols. A band at 1550 - 1580 cm^{-1} is assigned to the C–O vibration of the phenol.

An envelope of weak to strong intensity in the region of ~ 3450 cm^{-1} observed in the spectra of all the compounds (recorded as KBr discs) is due to the O–H stretches of the H_2O in the samples or in the KBr discs used. Usually no sharp O–H stretches could be distinguished. All of these copper complexes show a strong band, characteristic of the $\upsilon_3(ClO_4^-)$ vibration in the region of 1080 cm^{-1}. In some complexes this band is split implying that there is both ionic and bound ClO_4^- and that the ClO_4^- is involved in coordination which reduces the symmetry from tetrahedral.

3 : COMPLEXES OF LV5 and LV5t

3·1 : The Tetranuclear complexes of LV5

Complex **1**, $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot 4H_2O$, was obtained in ~ 40% yield from a number of reactions. Each time the analyses were in very good agreement with the above formula. The perchlorate bands in the IR (Fig. 3·2) are split which is consistent with perchlorate ions in more than one environment as explained above.

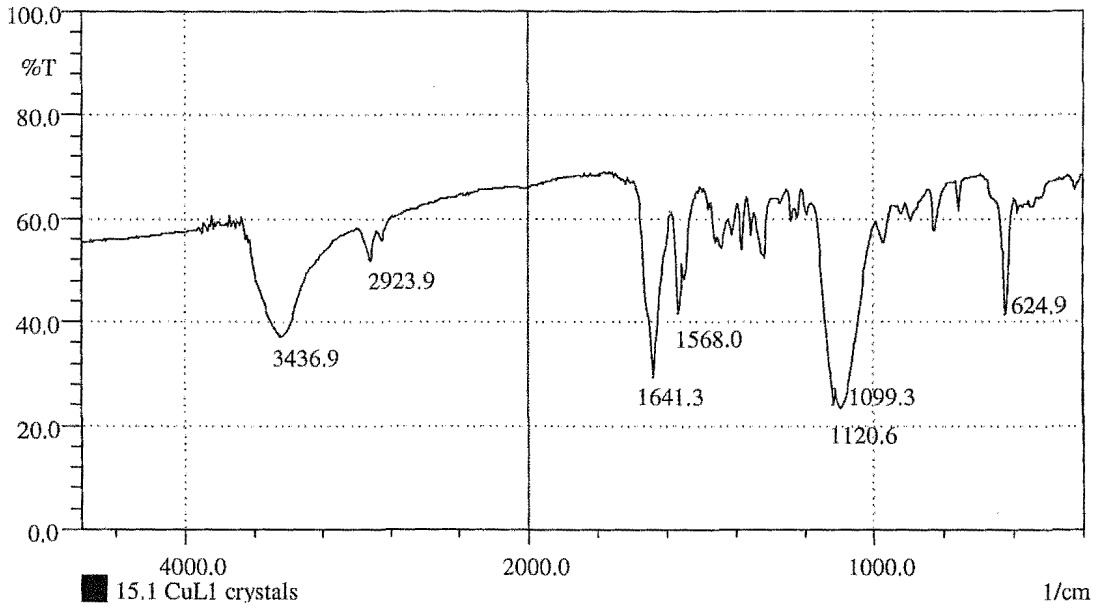


Fig 3·2 : Infrared Spectrum of Complex 1

Complex **2** was obtained after repeated recrystallisations of **1** by the diffusion of diethyl ether into a solution of **1** dissolved in acetonitrile. The structure of **2**, $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(CH_3CN)_3(ClO_4)_2]\cdot ClO_4\cdot H_2O$, was verified by X-ray crystal structure analysis and refined to R = 6·9%.

Four Cu(II) ions are bound within the **LV5** macrocycle, each coordinated to one imine N, one phenoxy O, one alkoxy O, the central hydroxide ion (Ox) and to one axial donor (CH_3CN or ClO_4^-). The macrocyclic oxygen donors are all deprotonated and each bridges two copper atoms, so that the square plane about each copper shares two edges with the equivalent plane of the neighbouring copper atoms. The Cu --- Cu distances [Cu(1) - Cu(2) 2·960(3), Cu(2) - Cu(3) 2·992(3), Cu(3) - Cu(4) 2·957(3) and Cu(4) - Cu(1) 2·974(3) Å] are quite short but non-bonding.[214] Bond distances between the copper atoms and the macrocyclic donors are unremarkable; however the significantly longer Cu - OH distances [Cu(1) and Cu(2) - Ox 2·117(8), Cu(3) - Ox 2·182(8) and Cu(4) - Ox 2·158(8) Å], coupled with compressed O - Cu - O angles (81·9 - 84·1°) suggest that this bond is weaker than the other three. This may be because of a slight mismatch between the central cavity size and the ideal length of a Cu - Ox bond or as a consequence of the unusual coordination about Ox. Three carbon atoms in the macrocyclic framework are disordered between two equivalent positions on either side of the macrocycle (Fig 3·3).

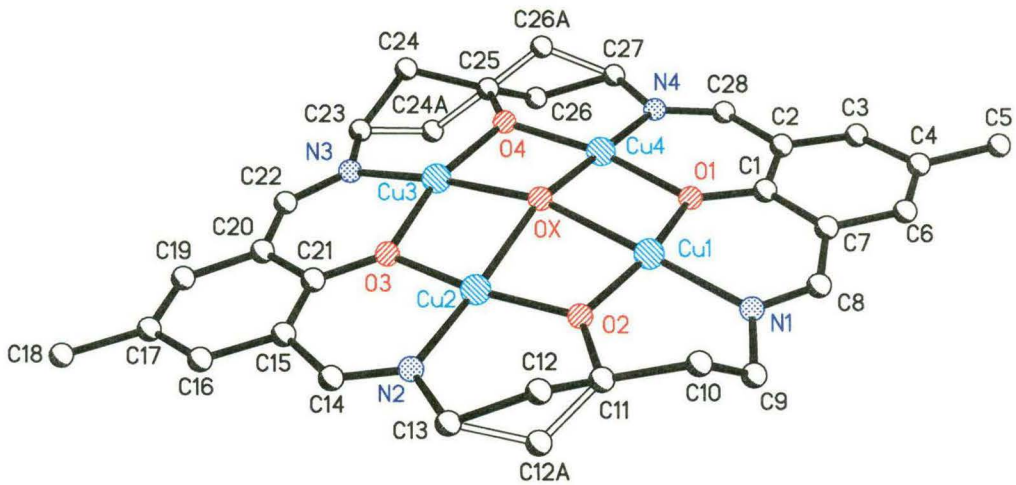


Figure 3·3 : The macrocycle core of complex 2 showing the disordered carbon atoms.

On one face of the macrocycle three of the coppers are bound to axial acetonitrile molecules and the remaining copper has a perchlorate ion associated with it. On the opposite face another perchlorate ion is bound, in a tripod fashion, to three of the copper ions (Fig. 3·4). This unusual binding was first reported in the description of the previously synthesised octacopper complex[43]. With the binding of CH_3CN and ClO_4^- groups to this molecule it has become a prototype structure in which different substrates are bound to one face of the copper array.

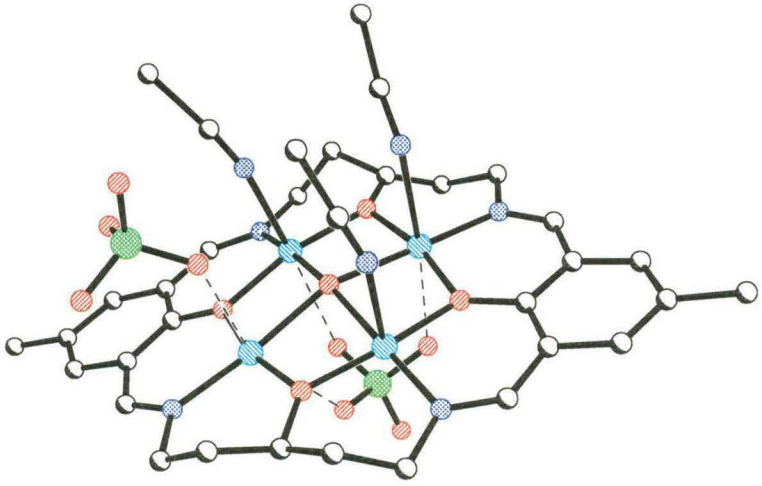


Figure 3·4 : Three acetonitrile ligands and two perchlorate ions are associated with the macrocyclic core of Complex 2

An unusual feature of this and related complexes is the bridging hydroxy group which sits 0·43 Å out of the plane of the four copper atoms (Fig. 3·6) with approximately square pyramidal geometry (including H as the fifth ligand).

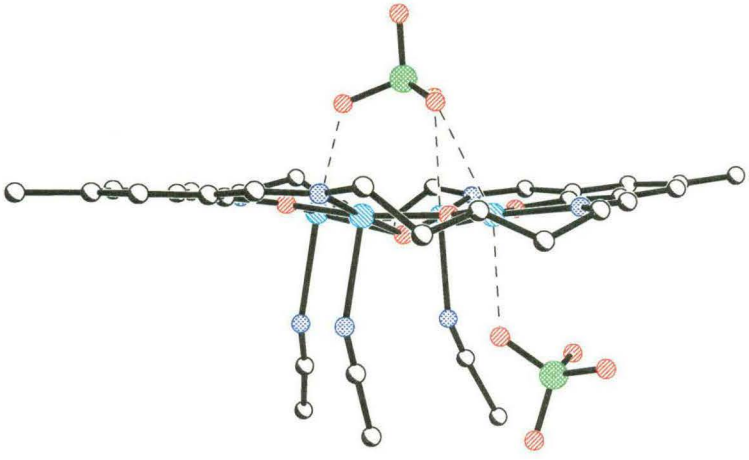


Figure 3·6 : Side view of Complex 2 showing the out-of-plane OH group.

The out of plane position of the central hydroxy group is more clearly seen in the thermal ellipsoid plot of the macrocyclic core (Fig. 3·7).

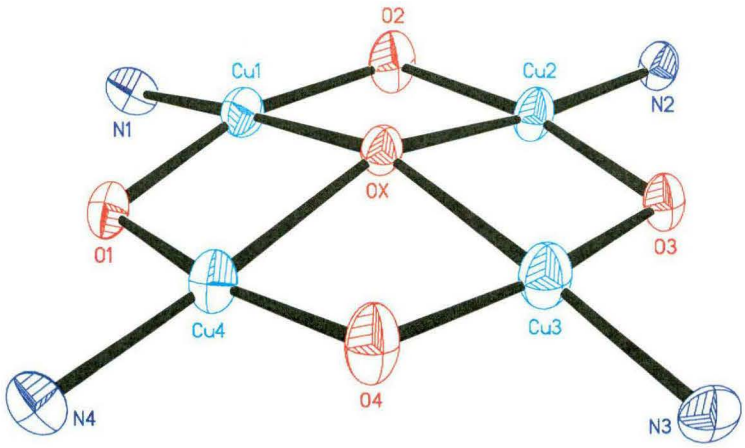


Figure 3·7 : Thermal ellipsoid plot of the out-of-plane OH group.

The contour map of this complex, in the plane of the four copper atoms (Fig 3·8), emphasises the deviation from the plane that this hydroxy group exhibits. The position of this group confirms the conclusion, from a previously published paper,[43] that the oxygen central donor, which was required by stoichiometry to have one negative charge and was therefore designated OH^-, was five coordinate and square pyramidal. In the previous complex, centrosymmetric symmetry required that the hydrogen atom be disordered above and below the plane of the macrocycle. If the oxygen has square-pyramidal geometry it would be expected to be slightly displaced from the plane of the copper atoms toward the proton. The centrosymmetric symmetry then requires that the oxygen be disordered between the positions above and below the ring. This was inferred by the elongation of the thermal ellipsoids in this direction relative to the other atoms of the core and is now confirmed by the out of plane position of the oxygen atom in the present non-disordered structure (Fig 3·9).

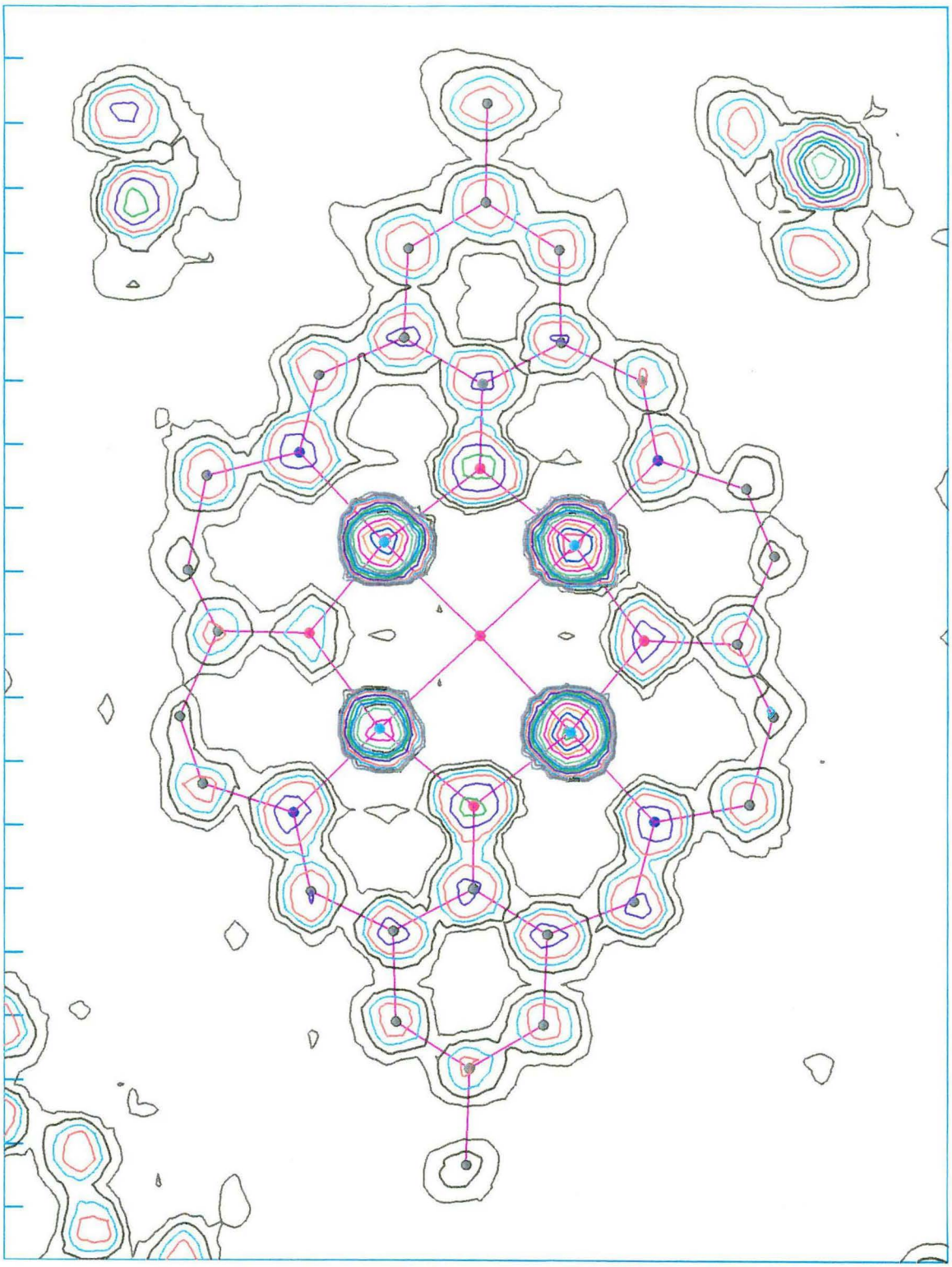


Figure 3·8 : Contour map through the plane of the four copper ions

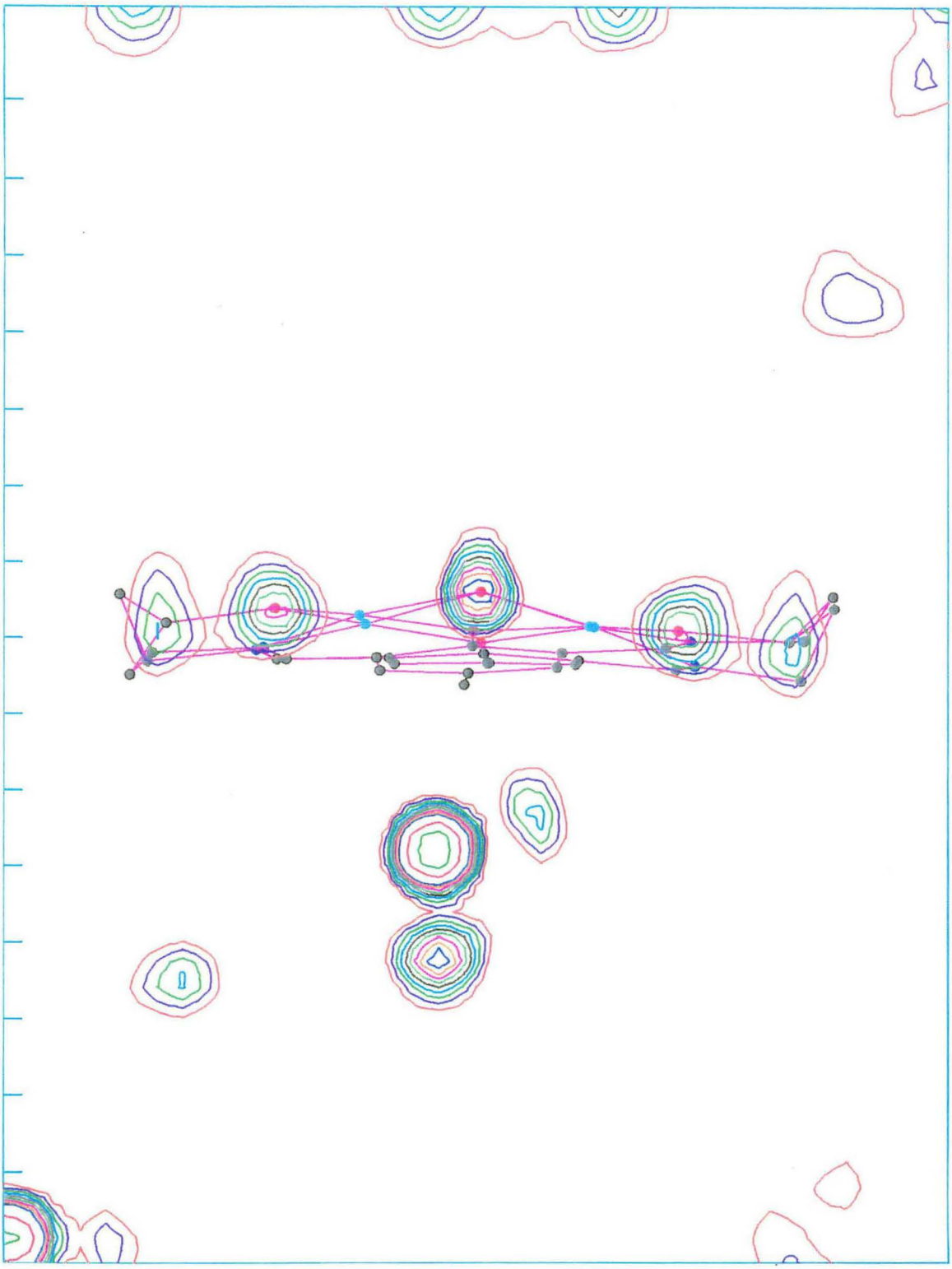


Figure 3·9 : Vertical contour map through two copper ions and the central hydroxide group

The packing diagram of this complex is shown in Figure 3·10. No bonding interactions between each discrete macrocyclic unit and its associated anions were found. The units are arranged in rows and are approximately perpendicular to the a axis. The macrocyclic units in one row are rotated by approximately 90° about the a axis to the units in the next row. No $\pi-\pi$ interactions were found with the distance between one phenol ring and its next nearest neighbour being ~6·2 Å.

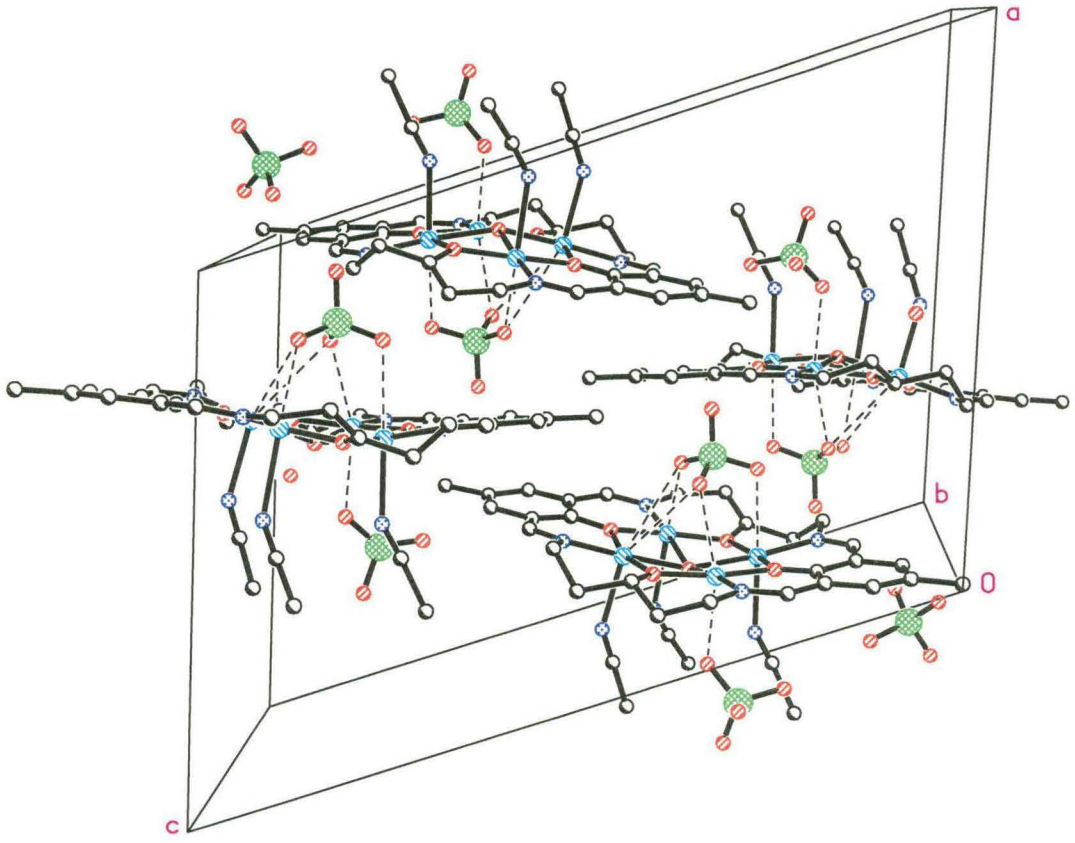


Figure 3·10 : Packing diagram of Complex 2

Table 3·1
Selected bond lengths (Å) and bond angles (°) for Complex 2

Cu(1)-O(2)	1·869(7)	Cu(1)-O(1)	1·911(7)	Cu(1)-N(1)	1·939(9)
Cu(1)-OX	2·119(6)	Cu(1)-N(60)	2·352(11)	Cu(1)-Cu(2)	2·962(3)
Cu(1)-Cu(4)	2·975(3)	Cu(2)-O(2)	1·856(6)	Cu(2)-O(3)	1·908(6)
Cu(2)-N(2)	1·936(8)	Cu(2)-OX	2·115(6)	Cu(2)-Cu(3)	2·991(2)
Cu(3)-O(4)	1·865(7)	Cu(3)-O(3)	1·919(6)	Cu(3)-N(3)	1·932(8)
Cu(3)-OX	2·178(6)	Cu(3)-N(70)	2·346(12)	Cu(3)-Cu(4)	2·959(3)
Cu(4)-O(4)	1·877(7)	Cu(4)-O(1)	1·912(6)	Cu(4)-N(4)	1·951(9)
Cu(4)-OX	2·156(6)	C(3)-C(4)	1·40(2)	O(80)-O(80A)#1	1·50(5)

O(2)-Cu(1)-O(1)	163·1(3)	O(2)-Cu(1)-N(1)	98·8(3)	O(1)-Cu(1)-N(1)	93·6(3)
O(2)-Cu(1)-OX	81·9(3)	O(1)-Cu(1)-OX	85·2(2)	N(1)-Cu(1)-OX	177·1(3)
O(2)-Cu(1)-N(60)	97·4(4)	O(1)-Cu(1)-N(60)	93·0(4)	N(1)-Cu(1)-N(60)	95·0(4)
OX-Cu(1)-N(60)	87·7(3)	O(2)-Cu(1)-Cu(2)	37·2(2)	O(1)-Cu(1)-Cu(2)	127·6(2)
O(2)-Cu(2)-O(3)	165·8(3)	O(2)-Cu(2)-N(2)	97·9(3)	O(3)-Cu(2)-N(2)	95·4(3)
O(2)-Cu(2)-OX	82·3(3)	O(3)-Cu(2)-OX	85·2(2)	N(2)-Cu(2)-OX	173·5(3)
O(4)-Cu(3)-O(3)	164·9(3)	O(4)-Cu(3)-N(3)	99·0(3)	O(3)-Cu(3)-N(3)	94·4(3)
O(4)-Cu(3)-OX	82·8(3)	O(3)-Cu(3)-OX	83·2(2)	N(3)-Cu(3)-OX	174·0(3)
O(4)-Cu(3)-N(70)	91·2(4)	O(3)-Cu(3)-N(70)	92·7(3)	N(3)-Cu(3)-N(70)	102·3(4)
O(4)-Cu(4)-O(1)	166·8(3)	O(4)-Cu(4)-N(4)	98·6(3)	O(1)-Cu(4)-N(4)	94·3(3)
O(4)-Cu(4)-OX	83·1(3)	O(1)-Cu(4)-OX	84·2(3)	N(4)-Cu(4)-OX	177·1(3)
Cu(2)-OX-Cu(1)	88·8(2)	Cu(2)-OX-Cu(4)	156·0(3)	Cu(1)-OX-Cu(4)	88·2(2)
Cu(2)-OX-Cu(3)	88·3(2)	Cu(1)-OX-Cu(3)	159·1(3)	Cu(4)-OX-Cu(3)	86·1(2)
OX-Cu(3)-N(70)	83·3(3)	C(1)-O(1)-Cu(4)	129·7(7)	C(1)-O(1)-Cu(1)	127·8(7)
Cu(4)-O(1)-Cu(1)	102·2(3)	C(11)-O(2)-Cu(1)	127·7(6)	C(11)-O(2)-Cu(2)	126·8(6)
Cu(1)-O(2)-Cu(2)	105·3(3)	C(21)-O(3)-Cu(2)	127·9(6)	C(21)-O(3)-Cu(3)	129·2(6)
Cu(2)-O(3)-Cu(3)	102·8(3)	C(25)-O(4)-Cu(4)	125·8(7)	C(25)-O(4)-Cu(3)	126·4(7)
Cu(4)-O(4)-Cu(3)	104·5(3)				

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z

Complexes **3**, **4**, **5t**, and **6t** (**t** = the tetranuclear precursors of the two octanuclear complexes) were assigned formulae on the basis of the IR (Table 3·2), FAB-ms (Table 3·3) and chemical analysis data.

Table 3·2 : Selected IR frequencies (cm^{-1}) for the copper complexes

1		3446		2923		1643	1567	1121		1089	627
2		3435		2924		1643	1566		1108	1090	625
3	3577	3427	3037	2928	1664	1633	1554		1103		626
4		3423		2924		1647	1551		1109	1090	626
5t*		3433		2918		1641	1560			1096	621
6t		3449		2920		1643	1567		1100		624
6		3384		2921		1646	1575			1082	623

* t = tetranuclear precursor

7	3437	3153		1632	1603	1543	1057	1036	534	523

The binuclear complex (**3**), $[Cu_2(H_4\mathbf{LV5})(ClO_4)_3Cl]\cdot 2H_2O$, was isolated from the filtrate of complex **1**. Although the chemical analysis could be made to fit formulae for both tetra- and binuclear complexes only peaks for binuclear fragments (Table 3·3) were found in the mass spectrum of this compound.

It appears that with copper the tetranuclear macrocyclic compound is easily formed, as even when this synthesis was carried out using just two metal equivalents,only a tetranuclear product **4**, $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot CH_3CH_2OH$ was ever isolated.

Table 3·3 : Selected FAB-ms ions for the copper complexes

		1	2	3	4	5(tet)	6(tet)	6
$Cu_4(O)$**LV5**$(ClO_4)_2ClOH$	1005·8		1005·8					
$Cu_4(OH)$**LV5**$(ClO_4)_2Na$	977·9	977·9				977·9	977·9	978
$Cu_4(OH)$**LV5**$(ClO_4)_2H$	955·8	958·9				958·9		
$Cu_2(H_4$**LV5**$)(ClO_4)_2Cl_2$	885·9			885·1				
$Cu_4(OH)$**LV5**Cl_3OH	878·9	878·0			880	878·0		
$Cu_2(H_4$**LV5**$)(ClO_4)_2ClOH$	868·0		868·8					
$Cu_4(OH)$**LV5**$(ClO_4)H$	856·9	857·0			857	857·0	856·9	859
$Cu_4(OH)$**LV5**Cl_2OH	843·9				843	841	840·9	841
$Cu_2(H_4$**LV5**$)(ClO_4)_2$	816·0			817·0				
$Cu_3(OH)(H$**LV5**$)(ClO_4)H$	796·1				796	796·1	796·0	
Cu_4**LV5**Cl	772·9							777
$Cu_4(OH)$**LV5**H	757·9	758·0	757·9			758·0	758·0	758
$Cu_2(H_4$**LV5**$)ClO_4ClH$	753·0			753·0	753			742
$Cu_2(H_4$**LV5**$)ClO_4$	717·1			716		715·1		717
$Cu_3(OH)(H$**LV5**$)H$	695·0	696·1			696	696·1	696·0	696
$Cu_3(H$**LV5**$)$	678·1	678					678·1	678
$Cu_2(H_2$**LV5**$)ClH_2$	653·1			653·1	653	653·1		
$Cu_2(H_4$**LV5**$)OH$	635·1		634					635
$Cu_2(H_2$**LV5**$)$	616·1		616·1	616·1	616	616·1	616·1	616·1

3·2 : The Octanuclear Complexes of LV5

Three methods were used to prepare octacopper complexes from their tetranuclear precursors. These included dissolving the tetranuclear precursor in methanol-dmf solutions of varying strengths and diffusing ether into these, treating a solution of a complex with triethylamine, and refluxing a methanolic solution with 2,6-diaminopyridine Two complexes **5**, $[\{Cu_4(\mu_5\text{-}O)$**LV5**$(ClO_4)\}_2]\cdot(ClO_4)_2\cdot 4H_2O$, and **6**, $[\{Cu_4(\mu_4\text{-}O)$**LV5**$(ClO_4)\}_2]\cdot[ClO_4\cdot Cl\cdot C_5H_7N_3]\cdot 2CH_3CH_2OH$, have been identified. Complex **6** formed in 51 % yield from a reaction in which the tetranuclear precursor was refluxed with the base 2,6-diaminopyridine and complex **5** by recrystallisation of a tetranuclear product from dmf. Complex **5** is very similar to that (complex **M9**) reported by M^{c}Kee[45] differing only in the number of water molecules trapped in the lattice.

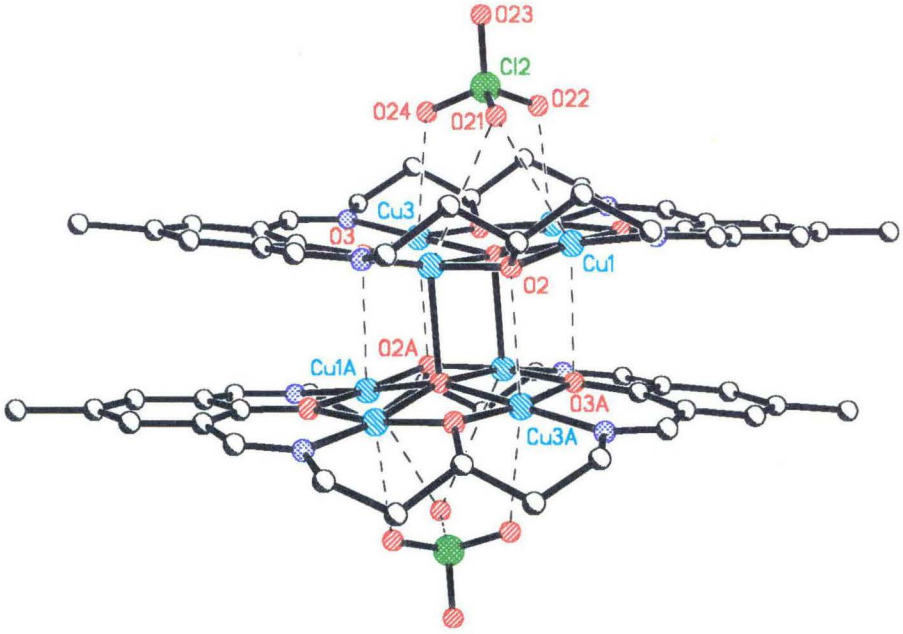


Figure 3·11 : Perspective view of the $[Cu_4(\mu_5\text{-}O)LV5(ClO_4)]^{2+}$ dimer of Complex 5

Figure 3·11 shows the X-ray crystal structure of the dimeric cation of $[Cu_4(\mu_5\text{-}O)\mathbf{LV5}(ClO_4)]^{2+}$ the dimeric cation of **5**. Within each macrocycle the arrangement is similar to that described for **2**; the four copper atoms are coplanar, and each is coordinated to an imine nitrogen atom, to bridging alkoxide and phenoxide donors, and to the central oxygen donor. The central oxygen is a five-coordinated oxo anion (Ox), which is displaced 0·279(7) Å from the mean plane of the four copper atoms. The coordination sphere of Ox is completed by Cu(2a) in the second macrocyclic unit. This bond and its symmetry equivalent, the Cu(2) - Ox(a) bond, hold the macrocycle together in a centrosymmetric dimer. There are also weaker links between Cu(1a) and O(3), Cu(3) and O(2a), and their symmetry equivalents.

A tripodially bound perchlorate anion is found on each face of the dimer. Perchlorate oxygen atoms O(24) and O(22) are each bound to one copper atom but O(21) is bound to two. The interatomic distances [O(24) — Cu(3) = 2·613(6) Å, O(22) — Cu(4) = 2·498(5) Å] are rather long, but are still within the range observed for axial copper-oxygen bonds.[214, 215] O(21) has longer interactions with Cu(2) [3·177(6) Å] and Cu(1) [2·874(6)]. M^{c}Kee[45] has pointed out that this inequivalence is not surprising as there is a general geometric

mismatch between the square-planar Cu_4 array and the tetrahedral perchlorate anion. However it must be noted that these linkages represent distinct bonding interactions and are not simply more generalised electrostatic interactions or crystal packing forces. This conclusion is supported by the observation that the shortest Cu — $O(ClO_4)$ distance involves Cu(4) which has no significant axial interaction on the other side of the macrocycle whereas the longest Cu — $O(ClO_4)$ distance is that to Cu(2), which has a strong axial bond to Ox(a).

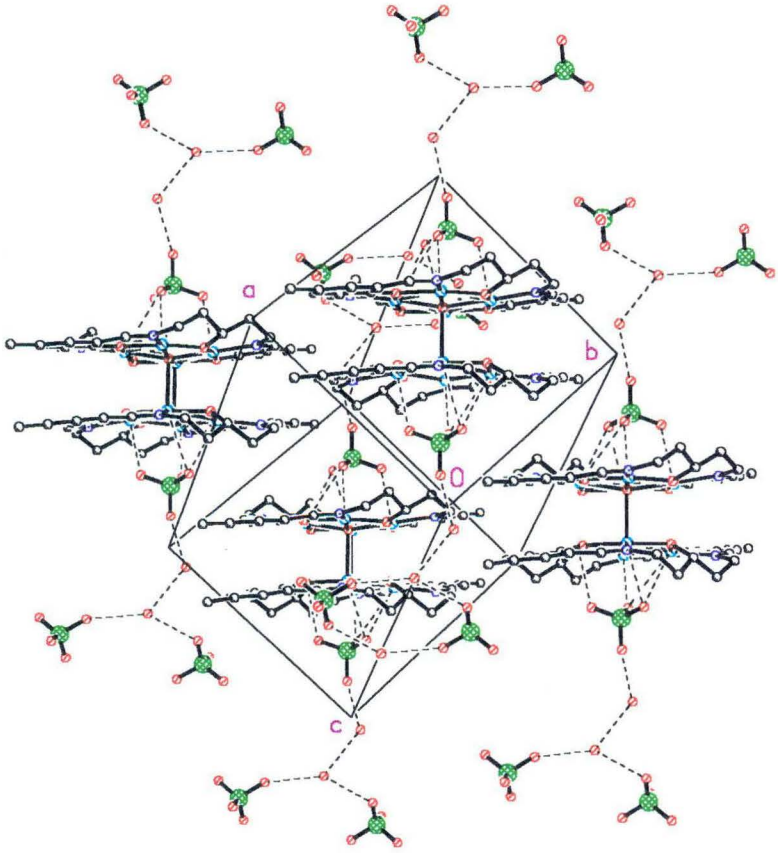


Figure 3·12 : Packing diagram of Complex 5

The packing diagram of Complex **5** (Fig. 3·12) shows that the macrocyclic dimers are arranged in columns with extensive hydrogen bonding within these columns. Each of the perchlorate anions, which is tripodially hydrogen bonded to the copper ions of the macrocycle, is also hydrogen bonded through the remaining oxygen to a water molecule. This water molecule (Fig. 3·13) is in turn hydrogen bonded to further water molecule which is part of an H-bonded dimer of two water molecules and two perchlorate anions.

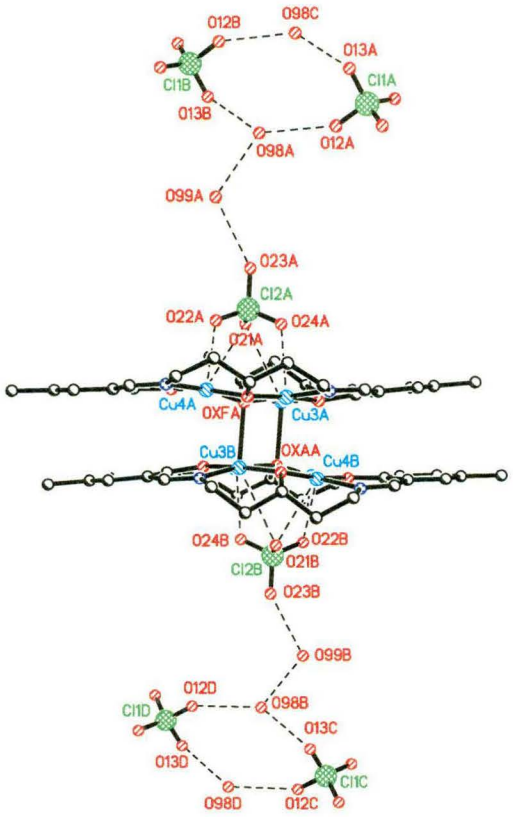


Figure 3·13 : Detail of hydrogen bonding interactions in Complex 5

This hydrogen bonding is very similar to that seen in $[\{Cu_4(\mu_4\text{-}O)LV5(BF_4)\}_2]\cdot(BF_4)_2\cdot 2H_2O$ (**M11**), an analogous octanuclear copper complex made using the BF_4^- anion (Fig. 3·14) and reported by Lingga. In the complex **M11** some of the BF_4 anions and the water molecules are linked in a very similar manner to the perchlorate complex.[204b]

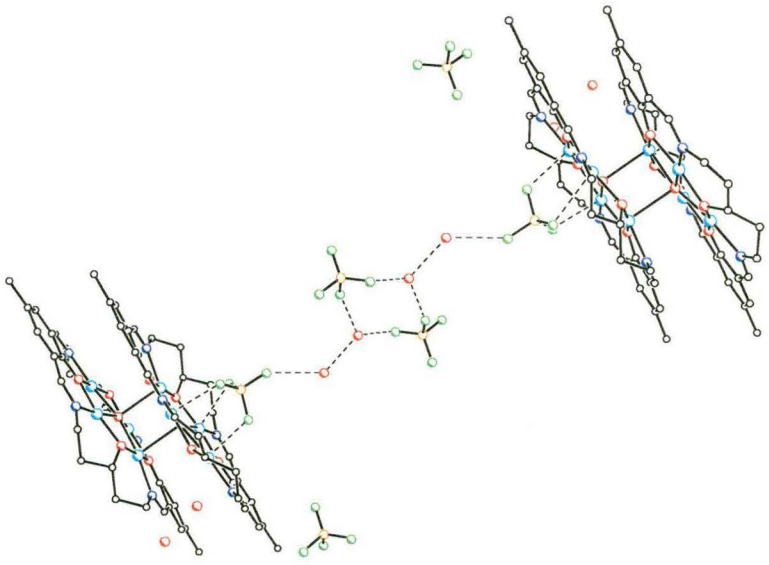


Figure 3·14 : Hydrogen bonding in $[\{Cu_4(\mu_4\text{-}O)LV5(BF_4)\}_2]\cdot(BF_4)_2\cdot 2H_2O$

Table 3·4a :

Selected bond lengths [Å] of Complex 5, $[\{Cu_4(\mu_5\text{-}O)LV5(ClO_4)\}_2]\cdot(ClO_4)_2\cdot 4H_2O$.

Cu(1)-O(2)	1·908(5)	Cu(1)-O(1)	1·909(5)	Cu(1)-N(1)	1·979(6)
Cu(1)-OX	2·032(5)	Cu(1)-Cu(2)	2·8535(14)	Cu(1)-O(21)	2·874(6)
Cu(1)-Cu(4)	2·888(2)	Cu(2)-O(2)	1·916(5)	Cu(2)-O(3)	1·937(5)
Cu(2)-N(2)	1·976(6)	Cu(2)-OX	2·065(5)	Cu(2)-OX#1	2·356(5)
Cu(2)-Cu(3)	2·923(2)	Cu(2)-O(21)	3·177(6)	Cu(3)-O(4)	1·892(5)
Cu(3)-O(3)	1·926(5)	Cu(3)-N(3)	1·976(6)	Cu(3)-OX	2·057(5)
Cu(3)-O(24)	2·613(6)	Cu(3)-O(2)#1	2·699(5)	Cu(3)-Cu(4)	2·849(2)
Cu(4)-O(4)	1·885(5)	Cu(4)-O(1)	1·904(5)	Cu(4)-N(4)	1·980(7)
Cu(4)-OX	2·062(5)	Cu(4)-O(22)	2·498(5)	OX-Cu(2)#1	2·356(5)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z

Table 3·4b :

Selected bond angles [°] of Complex 5, $[\{Cu_4(\mu_5\text{-}O)LV5(ClO_4)\}_2]\cdot(ClO_4)_2\cdot 4H_2O$.

O(2)-Cu(1)-O(1)	171·0(2)	O(2)-Cu(1)-N(1)	96·1(2)	O(1)-Cu(1)-N(1)	90·8(2)
O(2)-Cu(1)-OX	87·5(2)	O(1)-Cu(1)-OX	85·2(2)	N(1)-Cu(1)-OX	174·7(2)
O(2)-Cu(1)-O(21)	81·8(2)	O(1)-Cu(1)-O(21)	101·2(2)	O(4)-Cu(4)-O(1)	69.5(2)
N(1)-Cu(1)-O(21)	110·6(2)	OX-Cu(1)-O(21)	73·7(2)	Cu(2)-Cu(1)-O(21)	67·39(14)
O(2)-Cu(2)-O(3)	170·3(2)	O(2)-Cu(2)-N(2)	96·0(2)	O(3)-Cu(2)-N(2)	91·5(2)
O(2)-Cu(2)-OX	86·4(2)	O(3)-Cu(2)-OX	85·2(2)	N(2)-Cu(2)-OX	170·5(2)
O(2)-Cu(2)-OX#1	90·8(2)	O(3)-Cu(2)-OX#1	93.4(2)	N(2)-Cu(2)-OX#1	103.0(2)
OX-Cu(2)-OX#1	86·1(2)	O(2)-Cu(2)-O(21)	73·7(2)	O(3)-Cu(2)-O(21)	98·5(2)
N(2)-Cu(2)-O(21)	105·4(2)	OX-Cu(2)-O(21)	66·4(2)	OX#1-Cu(2)-O(21)	148·8(2)
Cu(1)-Cu(2)-O(21)	56·61(13)	Cu(3)-Cu(2)-O(21)	77·83(10)	O(4)-Cu(3)-O(3)	171·0(2)
O(4)-Cu(3)-N(3)	95·6(2)	O(3)-Cu(3)-N(3)	92·8(2)	O(4)-Cu(3)-OX	85·9(2)
O(3)-Cu(3)-OX	85·7(2)	N(3)-Cu(3)-OX	178·3(2)	O(4)-Cu(3)-O(24)	92·7(2)
O(3)-Cu(3)-O(24)	90·1(2)	N(3)-Cu(3)-O(24)	92·2(2)	OX-Cu(3)-O(24)	87·0(2)
O(4)-Cu(3)-O(2)#1	90·2(2)	O(3)-Cu(3)-O(2)#1	85·0(2)	N(3)-Cu(3)-O(2)#1	02·0(2)
OX-Cu(3)-O(2)#1	78·8(2)	O(24)-Cu(3)-O(2)#1	165·2(2)	O(4)-Cu(4)-N(4)	96·2(2)
O(1)-Cu(4)-N(4)	92·7(2)	O(4)-Cu(4)-OX	86·0(2)	O(1)-Cu(4)-OX	84·5(2)
N(4)-Cu(4)-OX	72·4(2)	O(4)-Cu(4)-O(22)	96·7(2)	O(1)-Cu(4)-O(22)	88·0(2)
N(4)-Cu(4)-O(22)	96·2(2)	OX-Cu(4)-O(22	90·7(2)	Cu(1)-OX-Cu(4)	89·7(2)
Cu(3)-OX-Cu(4)	87·5(2)	Cu(1)-OX-Cu(2)	88·3(2)	Cu(3)-OX-Cu(2)	90·3(2)
Cu(4)-OX-Cu(2)	166·5(3)	Cu(1)-OX-Cu(2)#1	99·3(2)	Cu(3)-OX-Cu(2)#1	98·6(2)
Cu(4)-OX-Cu(2)#1	99·6(2)	Cu(2)-OX-Cu(2)#1	93·9(2)	C(5)-O(1)-Cu(4)	130·9(4)
C(5)-O(1)-Cu(1)	130·7(4)	Cu(4)-O(1)-Cu(1)	98·5(2)	C(9)-O(2)-Cu(1)	124·2(4)
C(9)-O(2)-Cu(2)	126·6(4)	Cu(1)-O(2)-Cu(2)	96·5(2)	C(19)-O(3)-Cu(3)	129·5(4)
C(19)-O(3)-Cu(2)	129·9(4)	Cu(3)-O(3)-Cu(2)	98·3(2)	C(23)-O(4)-Cu(4)	125·7(5)
C(23)-O(4)-Cu(3)	127·5(5)	Cu(4)-O(4)-Cu(3)	97·9(2)		

The dimerisation of the tetracopper complex to form the octacopper equivalent was followed by monitoring the d - d band in the electronic spectrum. The solution spectrum, in fresh DMF, (Fig 3·15) of the tetracopper complex (λ_{max} 650nm) changes slowly over three days to be identical with that reported for the octacopper complex (λ_{max} 622 nm).[43] This spectral change can be accomplished in a few minutes by the addition of base. It has been shown[43] that the addition of a small amount of acid will readily reverse the process and provided the pH does not become too low, the tetra-, octa-, tetracopper cycle can be repeated a number of times without any apparent decomposition. If the pH becomes too low the ligand donors are protonated and the copper lost from the macrocycle.

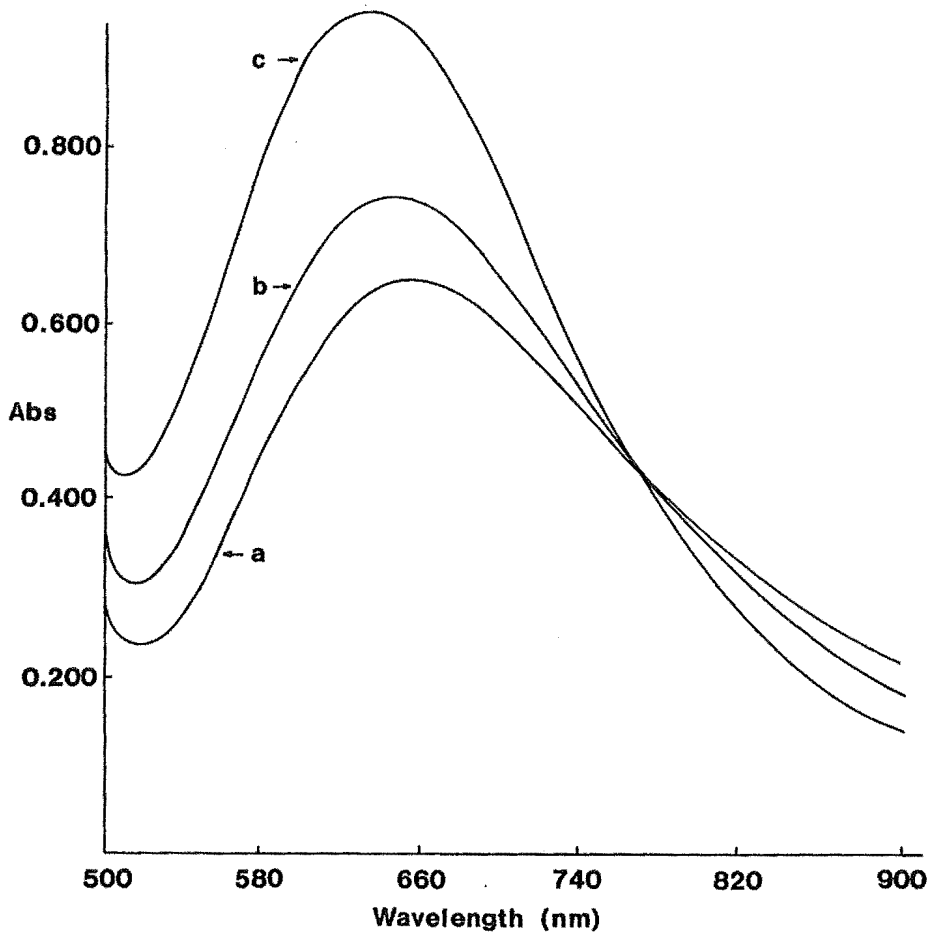
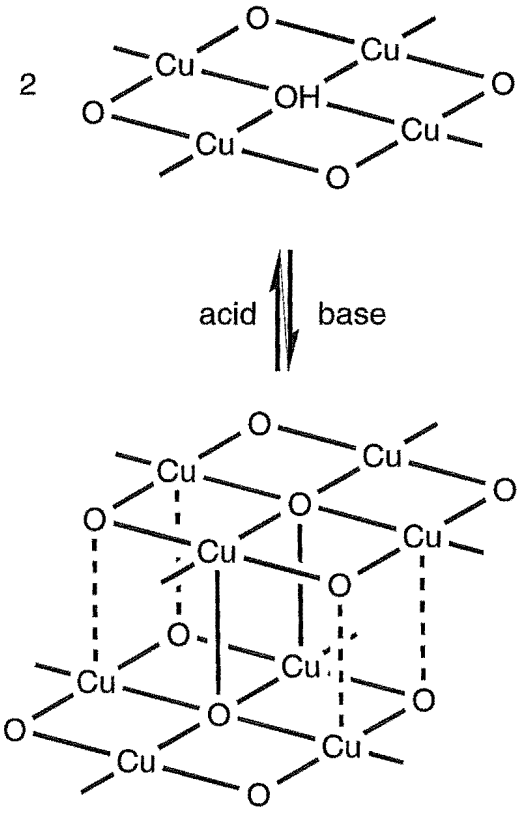


Figure 3·15 : The electronic spectrum of 1 in DMF; (a) fresh solution, (b) at T = 6 h, (c) at T = 36 h.

The dimerisation process can be explained in terms of competition between protons and macrocycle bound copper atoms for the central oxygen donor (Scheme 3·1). In more protic solvents such as ethanol the tetracopper monomer with the hydroxide at the centre is favoured. In DMF, which is a less protic solvent, the octacopper dimer is preferred but the rate of conversion is slow. Addition of base deprotonates the Ox, leading to rapid dimer formation.



Scheme 3·1

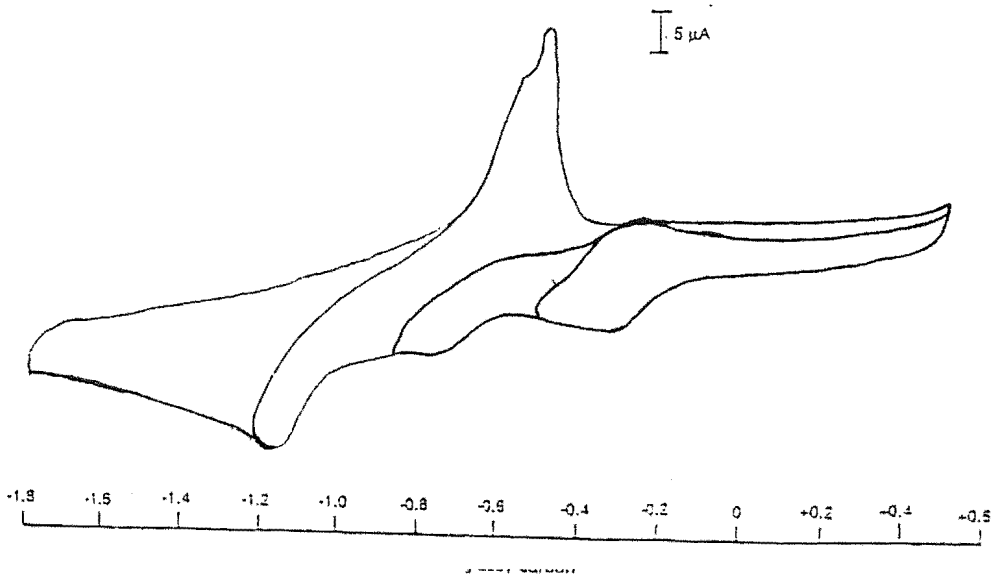
The treatment of the tetranuclear complexes with a variety of substances capable of binding to the open faces of the arrays was carried out. The crystal structure of **2** had shown that the binding of acetonitrile to the open face of complex **1** had occurred. Ethylene diamine was one of a number of other substances tried. A brilliant green solution of **1** in CH_3CN immediately changed to a deep moss green colour on addition of the ethylene diamine. Diffusion of ether into this solution produced tiny dark green crystals but unfortunately these could never be grown large enough to investigate with X-ray techniques. Comparison of the IR of these crystals with the IR of the original complex shows that a significant difference, apparently without disruption of the macrocycle, has been made to the original complex.

In all of the tetranuclear copper structures the $[Cu_4(\mu_4\text{-}OH)$**LV5**$]$ core is highly conserved. This fragment is seen in all of the FAB-ms spectra (Table 3·3). A readiness to swap axial ligands is demonstrated in many ways. For example, recrystallisation of complex **1** $[Cu_4(\mu_4\text{-}OH)$**LV5**$(ClO_4)_3]\cdot 4H_2O$, in CH_3CN led to

the formation of complex **2** $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(CH_3CN)_3(ClO_4)_2]\cdot H_2O$ in which three CH_3CN groups are now bound to copper ions. Treatment of complex **1** with a base, e.g diaminopyridine or dmf, led to the formation of a dimer in which one macrocyclic complex can be regarded as a ligand of the other with the central oxo as a donor atom. When a macrocyclic complex was treated with ethylene diamine changes in the IR spectrum indicated that the bound perchlorates had been displaced; probably by diamine ligands. The core structure is not only conserved but very stable. Treatment of the complexes in a variety of ways causes a variation in the superstructure and the solvates but does not disrupt the core.

3·3 : Electrochemistry of the Complexes

Electrochemical studies of this system were undertaken using Complex **1** dissolved in CH_3CN. The cyclic voltammogram of Complex **1** is shown in Figure 3·16. Chemically irreversible reduction steps are seen at E_p^c = -0·32 V, E_p^c = -0·74 V and E_p^c ~ -1·14 V. No other redox processes are seen within the solvent limit. There is a sharp oxidation peak at E_p^a = -0·5V associated with the reduction at E_p^c ~ -1·14V. Continuing the scan to more positive potentials shows a small quasi-reversible couple with $E_{½}$ = 0·75V.



Conditions : 10^{-3} complex, in CH_3CN, ν = 100 mVs^{-1} at glassy carbon, Area = 0·07 cm^3

Figure 3·16 : The cyclic voltammogram of the tetracopper complex 1

This couple ($E_{½}$ = 0·75V) observed using glassy carbon working electrode is more pronounced when the working electrode is platinum (Fig. 3·17).

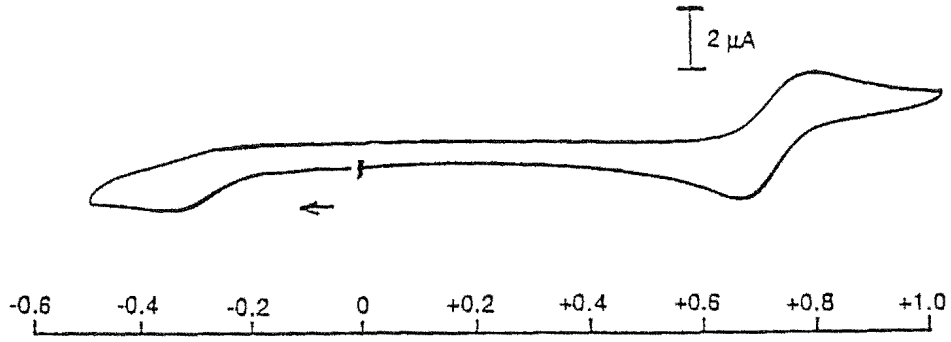


Figure 3·17 : Conditions : 10^{-3} complex, in CH_3CN, ν = 100 mVs^{-1} at platinum, Area = 0·03 cm^3

This couple is only seen when the potential is first scanned in the negative direction and hence arises from a reduction product (Fig. 3·18).

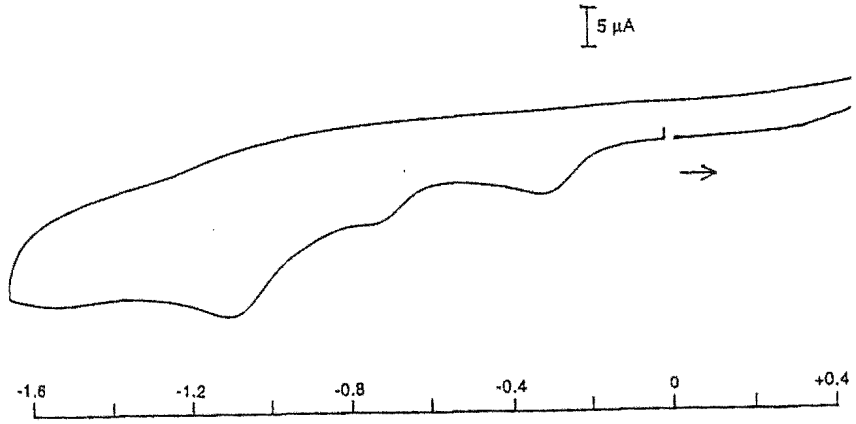


Figure 3·18 : Conditions : 10^{-3} complex, in CH_3CN, ν = 100 mVs^{-1} at glassy carbon, Area = 0·07 cm^3

The electrochemistry can be interpreted by reactions 1 - 5.

$$1.\ Cu_4\mathbf{LV5} + e^- \xrightarrow{E_p^c = -0{\cdot}32V} Cu_3\mathbf{LV5} + Cu(CH_3CN)_4^+$$

$$2.\ Cu_3\mathbf{LV5} + e^- \xrightarrow{E_p^c = -0{\cdot}74V} Cu_2\mathbf{LV5} + Cu(CH_3CN)_4^+$$

$$3.\ Cu(CH_3CN)_4^{+} + e^{-} \xrightarrow{E_p^c = -1{\cdot}14V} Cu(0)$$

$$4.\ Cu(0) \xrightarrow{E_p^a = -0{\cdot}5V} Cu(CH_3CN)_4^{+} + e^{-}$$

$$5.\ Cu(CH_3CN)_4^{+} \xrightarrow{E_{\frac{1}{2}} = 0{\cdot}75\ V} Cu(CH_3CN)_4^{2+} + e^{-}$$

The first two reduction steps (eqns 1 & 2) each result in loss of Cu(1) from the macrocycle and the current is consistent with a one electron process for each step. Cu(1) is stabilised by the formation of $Cu(CH_3CN)_4^{+}$ which is then reduced in the broad peak at ~ -1·14V (Eqn. 3). This results in deposition of Cu(0) on the electrode. The Cu(0) is stripped off giving the sharp oxidative peak at E_p^a = -0·5V (eqn. 4). The quasi-reversible couple with $E_{½}$ = 0·75 V corresponds to oxidation of $Cu(CH_3CN)_4^{+}$ (eqn 5). This interpretation is supported by the electrochemical behaviour of $Cu(ClO_4)_2$ in CH_3CN which was shown to undergo reactions 3 - 5 (Fig. 3·19).

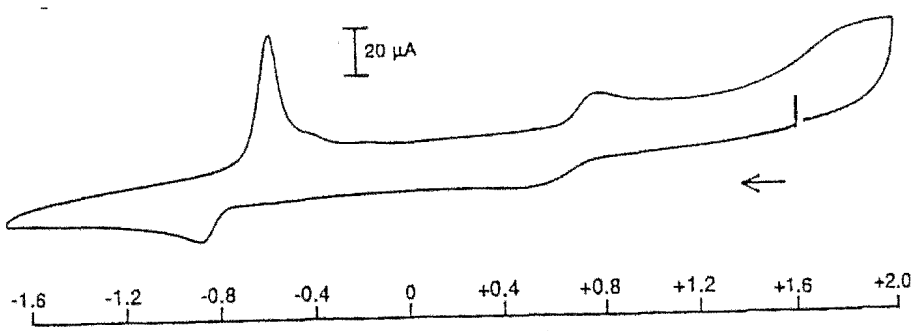


Figure 3·19 : Conditions : 10^{-3} $Cu(ClO_4)_2$, in CH_3CN, ν = 100 mVs^{-1} at glassy carbon, Area = 0·07 cm^3

Further, the electrochemistry of the complex in DMF has previously been investigated.[216] In contrast to the response in CH_3CN, all reduction steps resulted in deposition of Cu(0) on the electrode surface. This is consistent with disproportionation of Cu(I) which is lost from the macrocycle and which is not stabilised by complex formation in this medium. Reduction of the macrocycle leads to loss of Cu(I) from the macrocycle in both solvents.

In comparison, the electrochemistry of the octacopper complex (Fig. 3·20) is complicated. There is no loss of Cu(I) from the macrocycle as evidenced by the absence of an oxidative stripping peak from the cyclic voltammogram. This stabilisation in solution implies communication between the two macrocyclic units which comprise the halves of the dimer, i.e. the complex is not behaving as two monomers. Another consequence of the copper going from four to five coordinate geometry is a change in the reduction potentials of this complex from those of the tetranuclear complex.

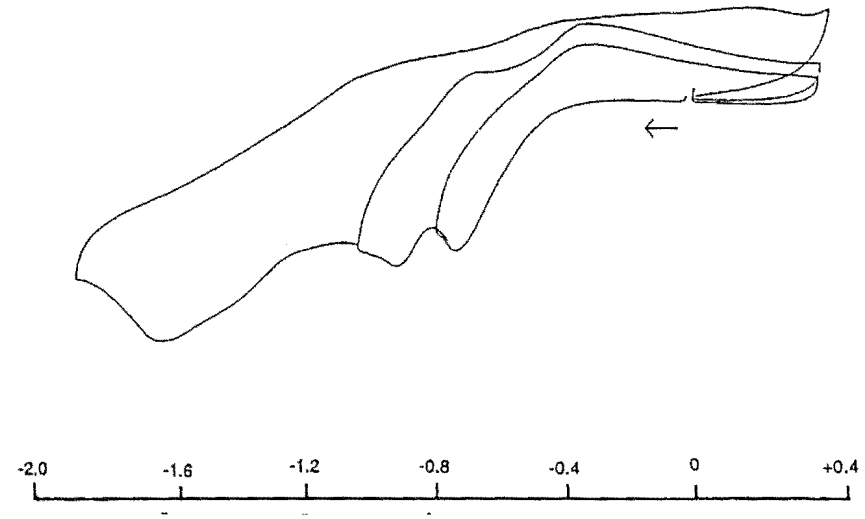


Figure 3·20 : Conditions : 10^{-3} complex, in dmf, ν = 200 mVs^{-1} at glassy carbon, Area = 0·07 cm^3

3·4 : Catalytic Activity of these Complexes

The use of the copper complexes as catalysts was investigated using the method of Malachowski *et. al.*[217] The oxidation of catechol to the quinone is investigated. Both the tetra- and octanuclear complexes were reacted with catechol and the changes over time monitored by UV. Addition of a methanolic catechol solution to solutions of the macrocycles always caused a marked and instant colour change from brilliant green to moss green. Within 90 minutes the solution was a green-brown colour. Figures 3·21a and 3·21b show the change over time of a solution of complex **1** treated with catechol.

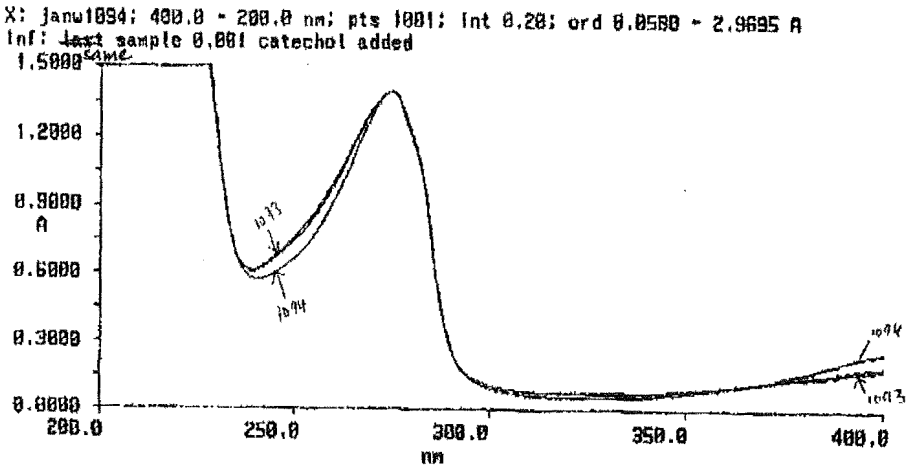


Figure 3·21a :

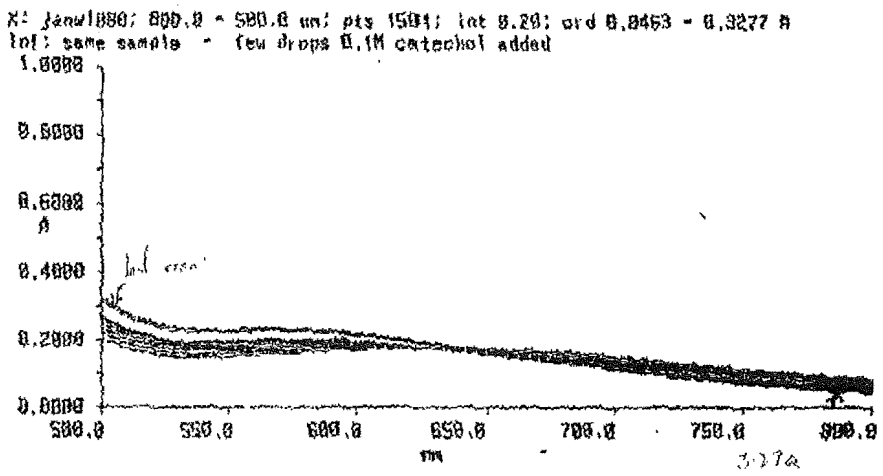


Figure 3·21b

A number of solid products were collected from various catechol-complex solutions and many of these were microcrystalline but the crystals were never able to be grown big enough for X-ray studies. The solids were always very dark brown or black. Figure 3·24a shows the IR of the product after treatment of complex **1** with catechol and comparison with the IR of the original complex (Fig. 3·24b) shows that significant changes have occurred. The chemical analysis of the product, while not definitive, indicates that one side of the macrocycle has been opened, two coppers have been lost from it and some catechol (or p-quinone) has bound in some way. The appearance of a peak at ~1603, indicative of unbound NH_2, supports this.

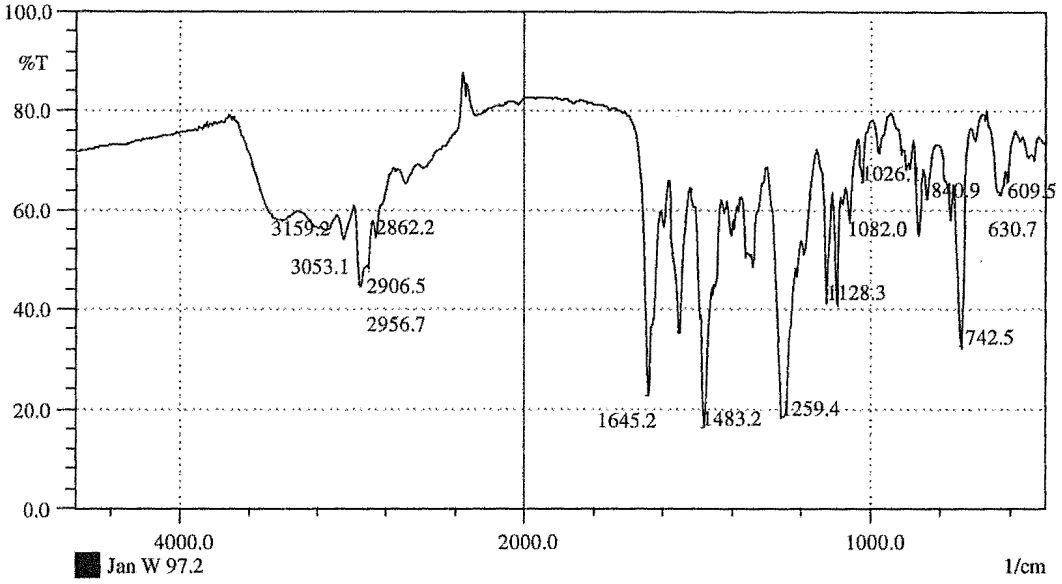


Figure 3·24a

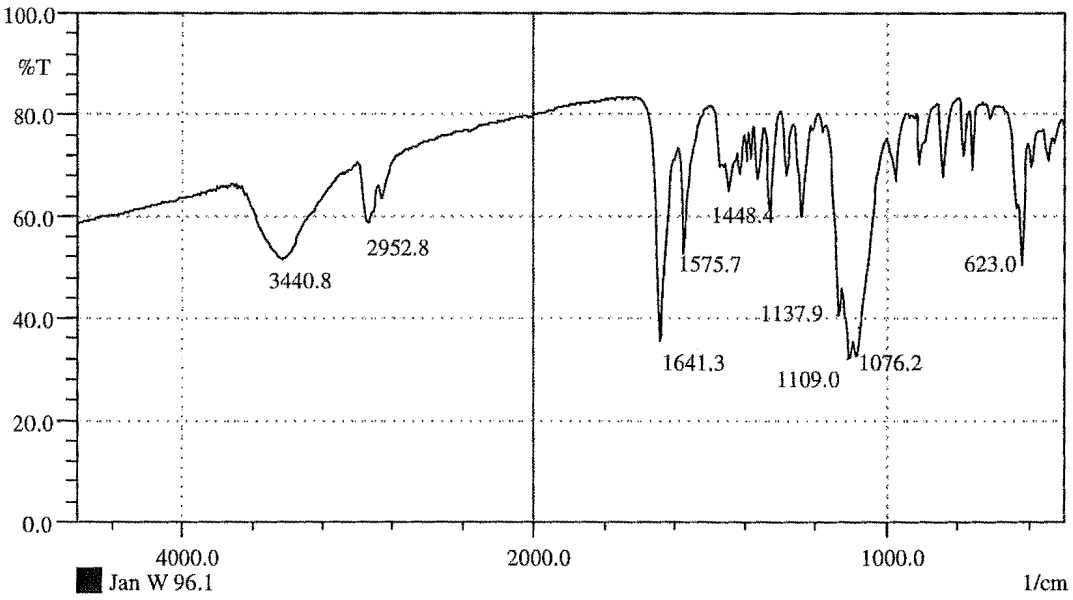


Figure 3·24b

The ability of these tetranuclear complexes to act as catalysts has been demonstrated[204c] in the slow hydrolysis of DMF to formate by complex **M12** Cu_4**LV5**$(OH)(BF_4)_3(H_2O)_2$. Slow evaporation of the DMF solution of complex **M12** gave complex **M13** [Cu_4**LV5**$(\mu_4$-OH)$(\mu$-HCOO)(OH)Cl]$\cdot 6H_2O$ (Fig. 3·22) which contains a formate ion bridging two of the copper(II) ions. The incorporation of a formate ion into the macrocyclic complex cation $[Cu_4$**LV5**$(OH)]^{3+}$ to give the formate bridged complex **M13** was unexpected as

neither a formate salt nor formic acid had been added to the solution of complex **M12**.

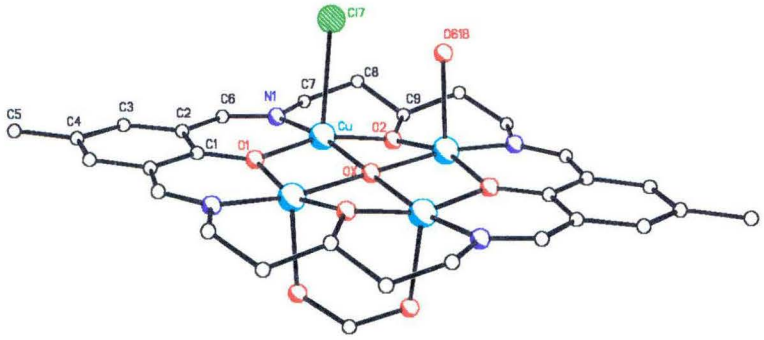


Figure 3·22 : The [Cu_4LV5(μ_4-OH)(μ-HCOO)(OH)Cl] core of complex M13

The crystal structure of **M13** (Fig. 3·22) revealed a μ-1,3 formate ion and a monodentate hydroxo ion coordinate axially to the surface of the planar Cu_4OH core. The μ-1,3 bridging mode of this formate ion is the same as that found in a dicopper(II) podal complex characterised by Karlin[218] and for which it is claimed that the formate was formed by the hydrolysis of DMF. The presence of the axial OH^- donor in **M13** suggests that some time hydroxo ions have coordinated to the Cu_4 surface of the cation $[Cu_4\mathbf{LV5}(\mu_4\text{-OH})]^{3+}$ of the **M12** precursor. Their most likely origin is from water molecules present in complex **M12** as water molecules of crystallisation or from water molecules in the atmosphere which came in contact with the DMF solution during the evaporation period.

DMF is a coordinating solvent, and a number of copper(II) complexes[119, 219] in which a DMF molecule coordinates to the metal ion through the aldehyde oxygen have been structurally characterised. Complex **2** (p.107), in which the planar $[Cu_4\mathbf{LV5}(\mu_4\text{-OH})]^{3+}$ core has three molecules of acetonitrile and one perchlorate ion coordinated to each copper(II) ion, demonstrates that this moiety is able to bind small molecules to its Cu_4 core. Hence it is quite likely that DMF and an OH^- ion are coordinated side-by-side to the cation $[Cu_4\mathbf{LV5}(\mu_4\text{-OH})]^{3+}$ of complex **M12** as illustrated in structure **I** of Figure 3·23.

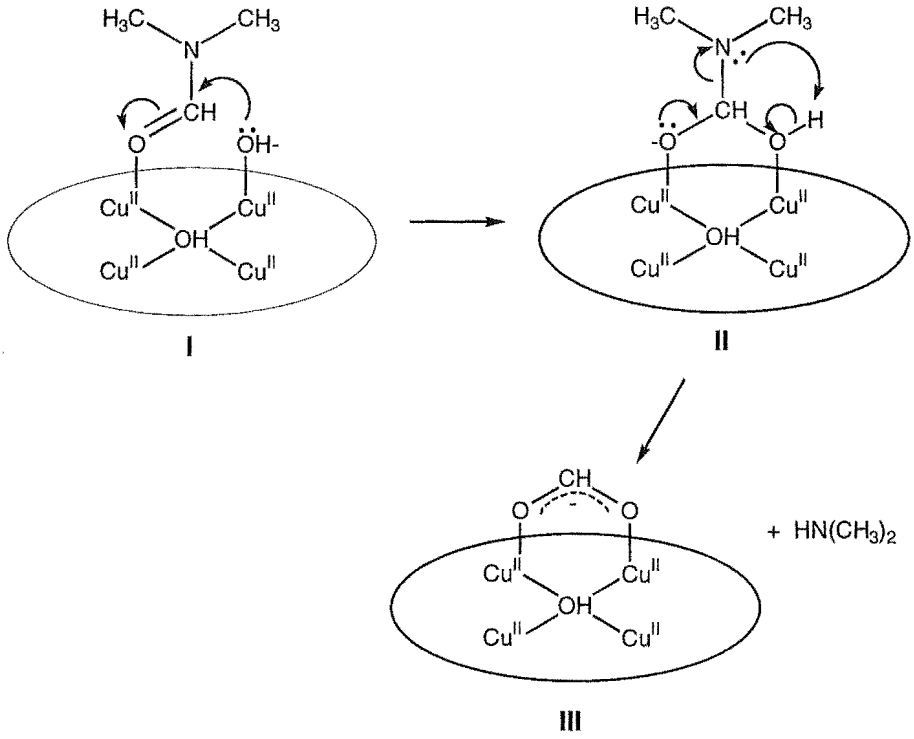


Figure 3·23 : Possible mechanism for the copper(II) catalysed hydrolysis of DMF by a tetracopper(II) complex of LV5⁻.

A subsequent nucleophilic attack by the hydroxo ion at the carbon atom of the coordinated DMF molecule would lead to the formation of a μ-1,3 $HCOO^-$ ion (structure **III** Figure 3·23). That is, it is possible that the formate ion in complex **M13** is the product of a slow hydrolysis of DMF solvent, catalysed by the tetracopper(II) complex cation $[Cu_4\mathbf{LV5}(\mu_4\text{-}OH)]^{3+}$.

4 : COMPLEX WITH THE TETRAFLUOROBORATE ANION

The normal reaction procedures, using dfmp and dtfp were carried out using copper tetrafluoroborate as the metal salt. In both cases the first product from the reactions were identified, by IR, to be predominantly inorganic. The filtrates were put aside for slow evaporation and eventually "dried" to a mixture of a sludge within which some deep green crystals were trapped. The crystalline material was separated out, redissolved in a boiling EtOH : MeOH mixture and set aside again for slow evaporation. This material was left for ten months and once again formed a "wet" mixture of sludge and a deep green crystalline material. Crystals separated from the dfmp mixture were investigated by X-ray

techniques. Although the crystals looked excellent they did not diffract well and the structure is only partially resolved. Attempts at recrystallisation of this material, in the hopes of being able to get a better data set, are being carried out.

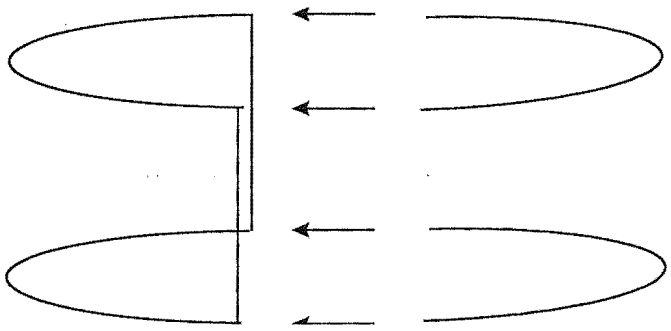


Figure 3·25 : Illustrating the fold of the macrocycle and the approach of the dfmp ligands

The macrocycle is folded in the manner shown in Figure 3·25. Two phenol dialdehydes have formed imine linkages as in a conventional macrocycle and the structure has then folded to allow two more unchanged phenol dialdehyde moieties to coordinate to each pair of copper ions. The two planar sections sit above, but not parallel to, each other. The result is a structure which resembles an open clam. Each of the copper atoms is five coordinate. A chlorine ion bridges between a copper atom in one section and another in the second section. The other copper in each section has a water molecule, which is directed away from the macrocyclic cavity, coordinated to it. Figure 3·26 shows the macrocyclic cation $[Cu_4(H_2\mathbf{LV5})(dfmp)_2Cl(H_2O)_2]^+$ viewed from the more open end.

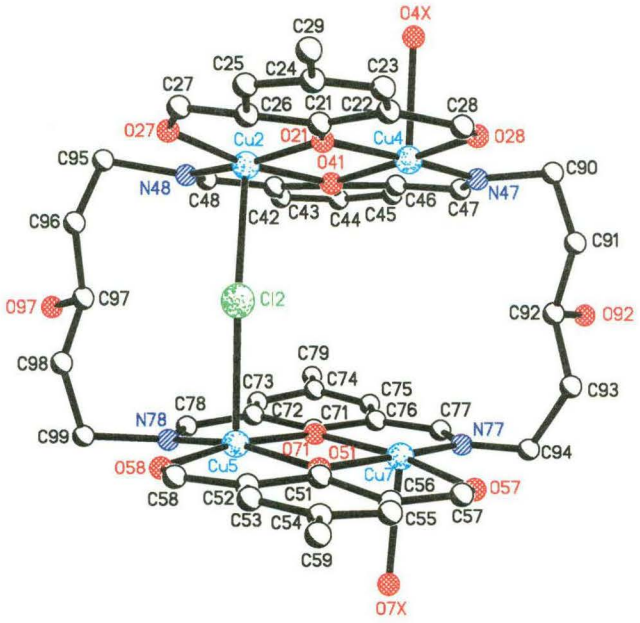


Fig 3·26 : One of the macrocyclic cations $[Cu_4(H_2LV5(dfmp)_2Cl(H_2O)_2]^+$ viewed from the "open" end

The side view of the complex **7** cation (Fig. 3·27) shows clearly how the two sections of the macrocycle, while being quite planar, are inclined at an angle of 17·9° to each other. It can also be clearly seen that the two OH groups on the diimine linking units are pointing in the same direction away from the chlorine.

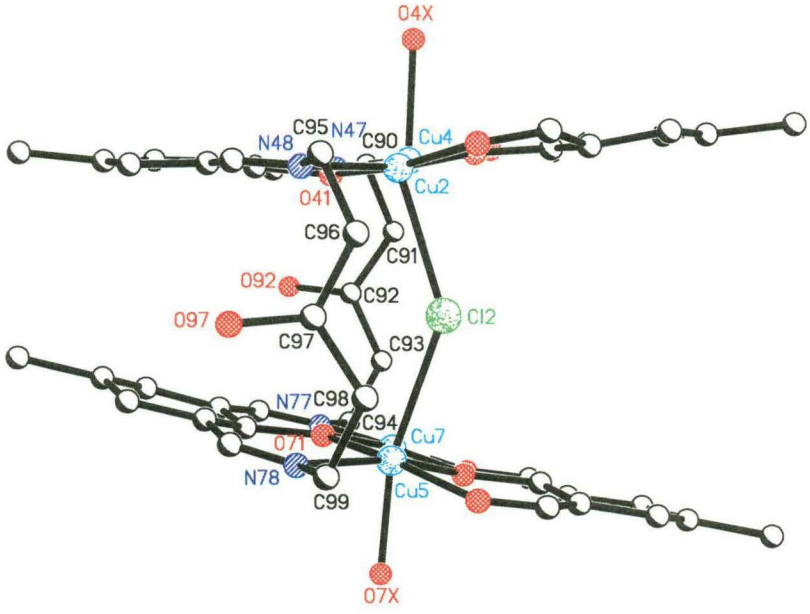


Figure 3·27 : The macrocyclic cation $[Cu_4(H_2LV5)(dfmp)_2Cl(H_2O)_2]^+$ showing the inclination of the planes of each section to each other.

A similar arrangement has been reported[31] in a the dicopper Schiff base macrocyclic complex (**M14**) shown in Figure 3·28*. The pyridine base macrocycle is folded in such a way that two azide molecules have been able to coordinate to the copper ions in an analogous manner to dialdehydes in complex **7**. A third azide bridges the two coppers whereas in complex **7** a chloride bridge is present.

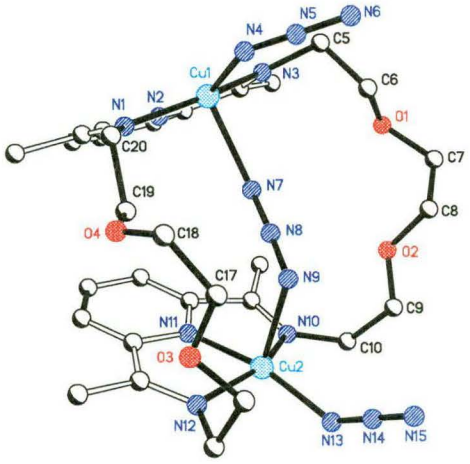


Figure 3·28 : The structure of $[Cu_2M13(N_3)_3]^+$

In complex **7** there are two macrocyclic cations in each unit cell and they are at approximate right angles (97·6°) to each other (Fig. 3·29). The unit cell also contains a number of solvent molecules and anions but these have not been fully resolved. The analysis results have been quite difficult to interpret but would indicate at least three BF_4^- units could be present. However it has recently been brought to the author's attention[220] that BF_3 and even B_2O units should also be looked for as the formation of these moieties from BF_4 is not unknown.

Conventional tetranuclear complexes have been made using the BF_4^- anion and the hydrogen bonding interactions (Fig 3·15) found in one of these has already been discussed.[206b]

* Refer also to Fig. 2b p4.

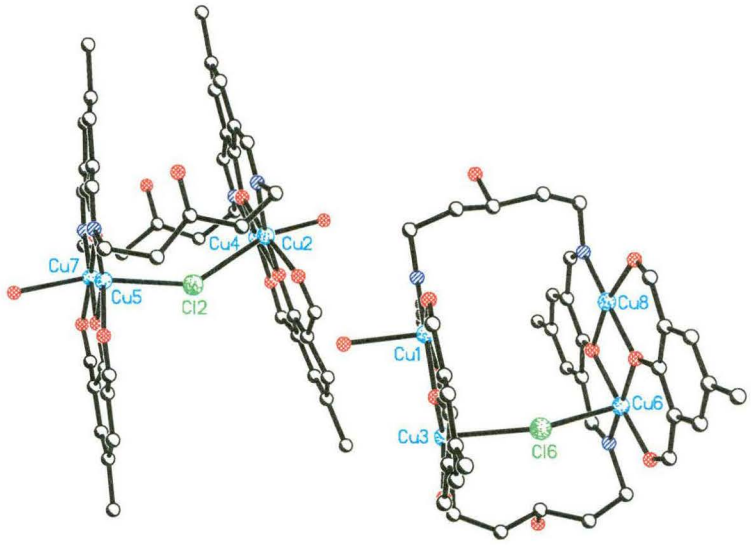


Figure 3·29 : Showing the orientation of the two macrocyclic cations to each other.

Table 3·5a : Selected bond lengths [Å] for Complex 7

Cu(2)-O(41)	2·01(12)	Cu(2)-N(28)	2·20(2)	Cu(2)-O(21)	2·00(13)
Cu(2)-O(47)	1·90(12)	Cu(2)-O(2X)	2·63(13)	Cu(2)-Cu(4)	3·02(4)
Cu(1)-N(38)	2·30(2)	Cu(1)-O(17)	1·94(12)	Cu(1)-O(11)	1·83(13)
Cu(1)-O(31)	2·20(2)	Cu(1)-Cl(1)	2·64(5)	Cu(1)-Cu(3)	3·03(3)
Cu(4)-N(27)	2·20(2)	Cu(4)-O(48)	2·03(13)	Cu(4)-O(21)	1·87(12)
Cu(4)-O(41)	1·80(14)	Cu(3)-O(18)	2·00(2)	Cu(3)-N(37)	2·10(2)
Cu(3)-O(31)	2·10(2)	Cu(3)-O(11)	1·91(13)	Cu(3)-O(3X)	2·3(2)
Cu(5)-O(58)	1·89(14)	Cu(5)-O(71)	1·9(2)	Cu(5)-O(51)	1·8(2)
Cu(5)-N(78)	1·80(2)	Cu(5)-Cl(1)	2·72(6)	Cu(5)-Cu(7)	3·02(4)
Cu(6)-O(87)	1·99(13)	Cu(6)-N(68)	2·10(2)	Cu(6)-O(81)	2·00(2)
Cu(6)-O(61)	1·7(2)	Cu(6)-Cl(6)	2·75(5)	Cu(6)-Cu(8)	2·97(4)
Cu(7)-N(77)	1·9(3)	Cu(7)-O(57)	2·10(2)	Cu(7)-O(51)	1·73(14)
Cu(7)-O(71)	2·3(2)	Cu(8)-N(67)	1·90(2)	Cu(8)-O(88)	1·86(14)
Cu(8)-O(81)	1·7(2)	Cu(8)-O(61)	2·17(14)		

Table 3·5b : Selected Bond Angles [°] for Complex 7

O(41)-Cu(2)-N(28)	154(7)	O(41)-Cu(2)-O(21)	72(5)	N(28)-Cu(2)-O(21)	82(7)
O(41)-Cu(2)-O(47)	99(6)	N(28)-Cu(2)-O(47)	108(8)	O(21)-Cu(2)-O(47)	161(6)
O(41)-Cu(2)-O(2X)	82(5)	N(28)-Cu(2)-O(2X)	98(6)	O(21)-Cu(2)-O(2X)	106(5)
O(47)-Cu(2)-O(2X)	89(5)	N(38)-Cu(1)-O(17)	99(6)	N(38)-Cu(1)-O(11)	160(6)
O(17)-Cu(1)-O(11)	95(6)	N(38)-Cu(1)-O(31)	83(6)	O(17)-Cu(1)-O(31)	173(6)
O(11)-Cu(1)-O(31)	82(6)	N(38)-Cu(1)-Cl(1)	107(5)	O(17)-Cu(1)-Cl(1)	89(5)
O(11)-Cu(1)-Cl(1)	88(4)	O(31)-Cu(1)-Cl(1)	97(4)	N(27)-Cu(4)-O(48)	93(7)
N(27)-Cu(4)-O(21)	99(7)	O(48)-Cu(4)-O(21)	167(6)	N(27)-Cu(4)-O(41)	171(8)
O(48)-Cu(4)-O(41)	88(6)	O(21)-Cu(4)-O(41)	80(6)	O(18)-Cu(3)-N(37)	108(8)
O(18)-Cu(3)-O(31)	171(5)	N(37)-Cu(3)-O(31)	80(8)	O(18)-Cu(3)-O(11)	91(6)
N(37)-Cu(3)-O(11)	161(8)	O(31)-Cu(3)-O(11)	82(6)	O(18)-Cu(3)-O(3X)	81(6)
N(37)-Cu(3)-O(3X)	92(7)	O(31)-Cu(3)-O(3X)	104(6)	O(11)-Cu(3)-O(3X)	90(6)
O(58)-Cu(5)-O(71)	180(7)	O(58)-Cu(5)-O(51)	98(7)	O(71)-Cu(5)-O(51)	82(8)
O(58)-Cu(5)-N(78)	96(10)	O(71)-Cu(5)-N(78)	84(10)	O(51)-Cu(5)-N(78)	160(10)
O(58)-Cu(5)-Cl(1)	90(5)	O(71)-Cu(5)-Cl(1)	90(5)	O(51)-Cu(5)-Cl(1)	89(5)
N(78)-Cu(5)-Cl(1)	106(7)	O(87)-Cu(6)-N(68)	100(8)	O(87)-Cu(6)-O(81)	92(7)
N(68)-Cu(6)-O(81)	166(8)	O(87)-Cu(6)-O(61)	171(7)	N(68)-Cu(6)-O(61)	89(8)
O(81)-Cu(6)-O(61)	80(7)	O(87)-Cu(6)-Cl(6)	89(5)	N(68)-Cu(6)-Cl(6)	96(5)
O(81)-Cu(6)-Cl(6)	91(4)	O(61)-Cu(6)-Cl(6)	91(5)	N(77)-Cu(7)-O(57)	104(10)
N(77)-Cu(7)-O(51)	157(10)	O(57)-Cu(7)-O(51)	99(7)	N(77)-Cu(7)-O(71)	85(10)
O(57)-Cu(7)-O(71)	170(6)	O(51)-Cu(7)-O(71)	73(7)	N(67)-Cu(8)-O(88)	95(9)
N(67)-Cu(8)-O(81)	174(9)	O(88)-Cu(8)-O(81)	91(8)	N(67)-Cu(8)-O(61)	99(8)
O(88)-Cu(8)-O(61)	164(7)	O(81)-Cu(8)-O(61)	75(6)	Cu(1)-Cl(1)-Cu(5)	142(2)

EXPERIMENTAL

1 : LV5 COMPLEXES WITH PERCHLORATES

1·1 : TETRANUCLEAR COMPLEXES

Complex 1 : $[Cu_4(\mu_4\text{-}OH)LV5(ClO_4)_3]\cdot 4H_2O$

$Cu(ClO_4)_2\cdot 6H_2O$ (4 mmol, 1·48 g) and dfmp (2 mmol, 0·324 g) were refluxed in hot dry EtOH (40 mL) for 10 mins. The dahp solution was made in 20 mL 1 :1 dry MeOH : EtOH. The reaction mix was refluxed 24 h and left stirring, while cooling, overnight. The solid was collected under vacuum.

Yield : 0·49 g, 0·38 mmol, 38 %

IR : 3442, 2923, 2855, 1642, 1560, 1093, 626 cm^{-1}

FAB-ms : 977·9(15), 958·8(10), 878·0(30), 857·0(100), 758·0(43), 696·1(32), 678(10)
997·9 : **LV5** + 4Cu + $2ClO_4$ + OH + Na
857·0 : **LV5** + 4Cu + ClO_4 + H_2O

Analysis for : $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot 4H_2O$

Calculated:	C : 29·47;	H : 3·46;	N : 4·58 %
Found:	C : 29·80;	H : 3·70;	N : 5·00 %

A bright green solution of **1** in CH_3CN was treated with ethylene diamine. An immediate colour change to a very deep moss green was observed. Ether was diffused into this solution and the resulting microcrystalline product collected. The crystals were too small for X-ray analysis but features in the IR show that significant changes had been made to the original complex.

Complex 2 : $[Cu_4(\mu_4\text{-}OH)LV5(CH_3CN)_3(ClO_4)_2]\cdot ClO_4\cdot H_2O$

Square green crystals of $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(CH_3CN)_3(ClO_4)_2]\cdot ClO_4\cdot H_2O$ were obtained after repeated recrystallisations of a solution made by dissolving Complex **1** $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot 4H_2O$ (0·155 g) in boiling CH_3CN and diffusing vapour of diethyl ether into this solution. The above formulation was verified by crystal structure analysis. The formulation below most closely matches the chemical analysis of crystals from the sample used for X-ray structure determination.

FAB-ms : 1005·8(9), 868·8(26), 757·9(27), 743·0(14), 634(22), 616·1(100)

Analysis for : $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot CH_3CN\cdot(C_2H_5OC_2H_5)\cdot 2H_2O$

Calculated :	C : 33·77;	H : 4·17;	N : 5·79 %
Found :	C : 33·80;	H : 4·20;	N : 5·80 %

Calculation for the found crystal structure would be :

Calculated :	C : 34·05;	H : 3·70;	N : 8·18 %

Complex 3 : $[Cu_2(H_4\mathbf{LV5})(ClO_4)_3Cl]\cdot 2H_2O$

The deep green filtrate of Complex **1** was set aside for slow evaporation and eight days later no solids had appeared. The frit which had been used to collect the original product was washed with DMF and the resulting solution was combined with the filtrate of Complex **1**. The solvents were removed under vacuum and the resulting solids dissolved in a minimum of boiling acetonitrile and this solution set aside for slow evaporation. After a further 9 days 0·05 g of green microcrystalline product was recovered.

IR : 3576, 3423, 3038, 2928, 1664, 1633 , 1555, 1103(pre sh), 626 cm^{-1}

FAB-ms : 885·1(2), 817·0(3), 753·0(40), 716(25), 653·1(68), 616·1(100), 555·2(44).

Analysis for : $[Cu_2(H_4\mathbf{LV5})(ClO_4)_3Cl]\cdot 2H_2O$

Calculated :	C : 33·99;	H : 4·07;	N : 5·66 %
Found :	C : 33·81;	H : 3·93;	N : 5·52 %

Complex 4 : $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot CH_3CH_2OH$

This complex was collected from a preparation in which only two equivalents of the metal salt were used. This preparation was part of an investigation in which the intention was to make binuclear complexes of the **LV5** ligand. The 2 mmol dahp was made in 20 mL dry MeOH : EtOH and added to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (2 mmol, 0·74 g) and dfmp (2 mmol, 0·324 g) which were mixed in hot dry EtOH (40 mL) and refluxed for 10 mins. The resulting bright green solution was refluxed for 20 h and allowed to cool to over 2 days. A dark forest green solid (some of which was semi-crystalline) was apparent and was collected by vacuum filtration.

Yield : 0·42 g, 0·40 mmol, 40 %

IR : 1646, 1551, 1109(spl), 1090, 626(spl) cm^{-1}

FAB-ms : 880(25), 857(31), 843(27), 796(28), 753(62), 696(50), 653(50), 616(100).

879·8 : **LV5** + 4Cu + 4Cl

616·1 : H_2**LV5** + 2Cu

Analysis for $[Cu_4\mathbf{LV5}(ClO_4)_3]\cdot CH_3CH_2OH$

Calculated:	C : 32·78;	H : 3·60;	N : 5·27 %
Found:	C : 33·00;	H : 3·61;	N : 5·17 %

However, an alternative could be

Analysis for $[Cu_4\mathbf{LV5}(ClO_4)_2Cl_2]\cdot CH_3OH\cdot H_2O$

Calculated:	C : 33·14;	H : 3·52;	N : 5·15 %

1·2 : THE OCTANUCLEAR COMPLEXES

The octacopper complexes were prepared in three ways with the third method being the most productive and consequently becoming the only method used.

Preparation 1 : A portion of the tetranuclear complex was dissolved in a minimum of 1 : 1 DMF : MeOH. Solutions for crystallisation were made up at three dilutions. The first one was the original solution, the second was 1 : 3 DMF : MeOH, and the third was diluted much more with MeOH.

Preparation 2 : A 1·58 x 10^{-3} mol L^{-1} solution of the tetranuclear complex **1** was made up in dmf and treated with an equimolar amount of triethylamine which was added from a syringe. The change over time was monitored by UV spectroscopy. Spectra recorded at time = 0, 2, 6, and 48 h and then daily for 17 days.

Preparation 3 : A portion of the tetranuclear complex was stirred in boiling MeOH and 2,6-diaminopyridine (dap) dissolved in the minimum of dry MeOH was added dropwise to the stirring ligand. The mixture was refluxed for 3 h and then left to cool with stirring overnight.

Complex 5 : $[\{Cu_4(\mu_5\text{-}O)\mathbf{LV5}(ClO_4)\}_2]\cdot 4H_2O$

Tetranuclear precursor : Dfmp and $Cu(ClO_4)_2$ were refluxed 10 mins in 40 mL dry EtOH. The dahp solution was made in 20 mL 1 : 1 dry MeOH : EtOH. The reaction mix was refluxed 24 h and left stirring, while cooling, overnight. The solid was collected in a frit. IR, FAB-ms, and chemical analysis showed this product to be $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot 4H_2O$ i.e the same as complex **1**

Yield : 0·49 g, 0·46 mmol, 46 %

IR : 3433, 2918, 2855, 1641, 1560, 1325, 1096, 899, 827, 762, 621 cm^{-1}

FAB-ms : 1368·8(2), 1267·9(2), 1167·0(4), 1068(3), 977·9(12), 958·9(7), 895(19), 878·0(38), 857·0(100), 841(27), 796·1(38), 758·0(30), 715·1(22), 696·1(68), 653·1(25), 616·1(55).

1368·6 : **LV5** + 4Cu + O + $6ClO_4$ + H_2O + H
856·9 : **LV5** + 4Cu + H_2O + ClO_4

Analysis for : $[Cu_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot 4H_2O$

Calculated :	C : 29·47;	H : 3·46;	N : 4·58 %
Found:	C : 29·39;	H : 3·41;	N : 4·65 %

All of this product was used, using the first two preparation methods, to make octacopper complexes of this ligand.

Preparation 1 :

The tetranuclear complex, 0·169 g was dissolved in ~3 mL of 1:1 DMF : MeOH. Solutions for crystallisation were made up at three dilutions. The first one was the original solution, the second was 1 : 3 DMF : MeOH, and the third was diluted much more with MeOH. Crystals of Complex **5** $[\{Cu_4(\mu_5\text{-}O)\mathbf{LV5}(ClO_4)\}_2]\cdot 4H_2O$ appeared in the first solution within a few hours.
They were characterised by X-ray crystal structure analysis.

Preparation 2 :

The tetranuclear product (0·196 g, 0·186 mmol) was dissolved in the minimum of DMF and treated with an equimolar amount of triethylamine (0·019 g, 0·186 mmol) which was added from a syringe. After the UV spectra had been taken the mixture was left in a small beaker covered with parafilm. After time a very dark green solid was observed in this and was collected by vacuum filtration.
IR : 3450, 2918, 2833, 2781, 1672, 1624, 1603, 1543, 1130, 1100, 1082, 959, 839, 772, 621.
FAB-ms : 1373·0(2), 1358·0(2), 1327·0(2), 1313·0(2), 1220·0(2), 1173·0(2), 1068(3), 919·1(3), 841·2(4), 823·2(6), 793·2(15), 777·2(3), 744·2(5), 732·1(3), 703·1(5), 686·1(15), 672·2(12), 656·0(10), 639·1(26), 534·0(100).

Complex 6 : $[\{Cu_4(\mu_4\text{-}O)LV5(ClO_4)\}_2]\cdot[ClO_4\cdot Cl\cdot C_5H_7N_3]$ $2CH_3CH_2OH$

Tetranuclear precursor : The usual procedure for the tetranuclear reaction was followed. The product, a dark green powder with darker green flaky material in it, was identified by IR.

Yield : 0·47 g, 0·44 mmol, 44 %

IR : 3449, 2920, 1643 , 1567, 1100, 624 cm^{-1}

FAB-ms : 977·9(30), 856·9(100), 840·9(40), 796·0(35), 758·0(85), 696·0(100), 678·1(35), 635·1(20), 616·1(100).

977·9 : **LV5** + 4Cu +2ClO_4 + OH + Na
856·9 : **LV5** + 4Cu + ClO_4 + H_2O
696·0 : H**LV5** + 3Cu + H_2O
616·1 : H_2**LV5** + 2Cu

Octacopper complex : The tetranuclear compound (0·419 mmols, 0·443 g) was stirred in 50 mL of boiling MeOH. 2,6-Diaminopyridine (0·837 mmols, 0·091 g) was dissolved in the minimum (~ 2 mL) of dry MeOH and added dropwise to the stirring ligand. The mixture was refluxed for 3 h and then left to cool with stirring overnight. The product, an extremely fine very dark green powder complex **6** was collected by vacuum filtration.

Yield : 0·40 g, 0·21 mmols, 51 %

IR : 3384, 2921, 2856, 1646, 1575, 1550, 1082, 638, 623 cm^{-1}

FAB-ms : 978(45), 897(15), 859(30), 841(10), 777(15), 758·0(100), 742(22), 717(15), 696(10), 678(8), 635(15), 616·1(90).

977·9 : **LV5** + 4Cu +2ClO_4 + OH + Na

616·1 : H_2**LV5** + 2Cu

Analysis for : $[\{Cu_4(\mu_4\text{-}O)\mathbf{LV5}(ClO_4)\}_2]\cdot(ClO_4)_2$

Calculated :	C : 35·10;	H : 3·40;	N : 5·90 %
Found :	C : 35·00;	H : 3·52;	N : 6·66 %

2 : LV5 COMPLEXES WITH TETRAFLUOROBORATE

2·1 : Cu - LV5 - BF_4

$Cu(BF_4)_2$ (1·381 g, 4 mmol) was dissolved in 40 mL and the dfmp (2 mmol) in 20 mL of dry EtOH, the two solutions were mixed and the deep green solution refluxed for 15 mins. The 2 mmol dahp solution was added dropwise and the resulting green-brown solution refluxed for 24 h. The reaction mixture had some solid around the solvent line. This solid, which is still unidentified, (0·311 g) was collected by vacuum filtration and the filtrate set aside for slow evaporation.

Over a period of weeks the filtrate produced a few green crystals around the side of the flask. Some of the green crystals were investigated for X-ray analysis but were not suitable. The remainder of the green crystals and some of the pale green sludge in the flask was redissolved in a MeOH : EtOH mix and left for slow evaporation. Eventually this dried to a lump which took the form of a "wet" mixture of green crystals and powder.

IR : 3470, 3170, 1634, 1603, 1333, 1236, 1034(spl), 887, 760, 635

FAB-ms : 1084·9(5), 921·9(5), 603·0(2), 529·9(100), 468(66), 451·8(88).

1085·9 : **LV5**$(dfmp)_2$ + 4Cu + 3O

923·9 : **LV5**(dfmp) + 4Cu + Cl

Chemical analysis of this product indicated that it was not homogenous. The green crystals were separated by hand, dissolved in DMF and set up for ether diffusion. The remaining material was dissolved in a boiling EtOH : MeOH mix and after considerable time when the solvent had almost completely evaporated away the flask contained dark green cubic crystals trapped in furry green "wet" deposits. X-ray investigation of the dark green chunks showed them to be Complex **7**. Other crystals in the flask took the form of blue-green needles and were not suitable for X-ray structure analysis..

All of the dark green crystals, not used for X-ray analysis, was redissolved in CH_3CN and filtered. The mixture was taken down to dryness and further dried under vacuum. IR and chemical analysis was carried out on this treated material.

IR : 3153, 1632, 1603, 1057, 1036.

FAB-ms : 1086·4(10), 848·5(10), 634·7(26), 580·8(58), 560·8(38), 529·7(74), 513·6(42), 467·8(100).

1085·9 : **LV5**$(dfmp)_2$ + 4Cu + O

No close match has been able to be made for the chemical analysis.

CRYSTALLOGRAPHY

Complex 2 : $[Cu_4(\mu_4\text{-}OH)LV5(CH_3CN)_3(ClO_4)_2]\cdot ClO_4\cdot H_2O$

Empirical formula	$C_{34}H_{34}Cl_3Cu_4N_7O_{14}$	
Formula weight	1120·84	
Temperature	193 K (-90°C)	
Crystal colour	dark green	
Crystal form	irregular cuboid	
Crystal size	0·8 x 0·6 x 0·4 mm^3	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 15·745(7) (Å)	$\alpha = 90°$
	b = 14·195(10) (Å)	$\beta = 110·60(5)°$
	c = 22·48 (2) (Å)	$\gamma = 90°$
Volume, Z	4702(6) $Å^3$, 4	
Density (calculated)	1·667 Mg m^{-3}	
Absorption coefficient	2.036 mm^{-1}	
F(000)	2356	
Theta range for data collection	4 to 45.00	
Scan Speed	4.88° $min.^{-1}$ in ω	
Scan Range (ω)	2·00°	
Background measurement	0.15	
Limiting indices	$-16 \leq h \leq 15$, $0 \leq k \leq 15$, $0 \leq l \leq 24$	
Reflections collected	6698	
Independent reflections	6136	
Refinement Method	Full-matrix least-squares	
Goodness-of-fit on F^2	2·56	
Observed Reflections	3755 ($F \rangle 6.0\sigma(F)$)	
Final R indices [$F>6\sigma(F)$]	R1 = 0·069, wR2 = 0·0916	
R indices (all data)	R1 = 0·1075, wR = 0·0978	
Largest diff. peak and hole	1·32 and -0·63 e.$Å^{-3}$	
Number of Parameters Refined	573	

Complex 5 : $[\{Cu_4(\mu_5\text{-}O)LV5(ClO_4)\}_2]\cdot(ClO_4)_2\cdot 4H_2O$

Empirical formula	$C_{28}H_{33}Cl_3Cu_4N_4O_{17}$	
Formula weight	1058·09	
Temperature	130(2) K	
Crystal colour	green	
Crystal form	block	
Crystal size	0·58 x 0·16 x 0·08 mm^3	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 11·423(2) Å	α = 102.95(3)°
	b = 12·706(3) Å	β = 113.08(3)°
	c = 13·497(3) Å	γ = 100.07(3)°
Volume, Z	1679·2(6) $Å^3$, 2	
Density (calculated)	2·093 Mg m^{-3}	
Absorption coefficient	2·826 mm^{-1}	
F(000)	1064	
Theta range for data collection	2·01 to 25·00°	
Scan Speed	6.00° $min.^{-1}$ in ω	
Scan Range (ω)	1.50°	
Background measurement	0.30	
Limiting indices	$0 \le h \le 12$, $-14 \le k \le 14$, $-16 \le l \le 14$	
Reflections collected	5981	
Independent reflections	5606 [R(int) = 0·0382]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5605 / 94 / 469	
Goodness-of-fit on F^2	1·071	
Final R indices [$I>2\sigma(I)$]	R1 = 0·0545, wR2 = 0·1429	
R indices (all data)	R1 = 0·0905, wR2 = 0·1651	
Largest diff. peak and hole	1·370 and -0·905 $e.A^{-3}$	

Complex 7 : $[Cu_4(H_2LV5)(dfmp)_2Cl(H_2O)_2]^+$

Temperature	190(2) K
Crystal colour	bright green
Crystal form	irregular cuboid
Crystal size	0·68 x 0·56 x 0·40 mm^3
Crystal system	monoclinic
Space group	P_1
Unit cell dimensions	a = 13·149(11) (Å) α = 97·60(4)°
	b = 20·881(11) (Å) β = 104·13(8)°
	c = 23·057(14) (Å) γ = 102·22(8)°
Volume, Z	5886(7) $Å^3$, 6
Density (calculated)	1.390 Mg m^{-3}
Absorption coefficient	1.69 mm^{-1}
F(000)	2432
Theta range for data collection	2 to 19°
Scan Speed	14 ° $min.^{-1}$ in ω
Scan Range (ω)	3.0 °
Background measurement	0.10
Limiting indices	$-9 \leq h \leq 9$, $-18 \leq k \leq 18$, $-21 \leq l \leq 21$
Reflections collected	9226
Independent reflections	8597 [R(int) = 0.4032]
Refinement Method	Full-matrix least-squares
Data / restraints / parameters	8597/0/573
Goodness-of-fit on F^2	1.967
Final R indices [F>4σ(F)]	R1 = 0.2249, wR2 = 0.5511
Largest diff. peak and hole	3.07 and -1.23 e.$Å^{-3}$

CHAPTER 4

THE TETRANUCLEAR COBALT COMPLEXES

1 : INTRODUCTION

The cobalt work has formed the largest part of this project and will be reported in two chapters. The acetate, chloride, nitrate, perchlorate, and thiocyanate salts of cobalt were used to make complexes with the **LV5** and **LV5t** ligands.

In contrast to the copper compounds, which formed planar tetranuclear complexes with open faces, the tetranuclear cobalt complexes of **LV5** characterised, prior to the beginning of this study, all contained acetate bridges. Therefore, one of the main aims of the synthetic work of this project was to make tetranuclear species without bridging acetate groups. The acetate containing structures are not planar and it is thought that the "bite" of the acetate bridges might be controlling the geometry of these complexes.

2 : SYNTHESIS

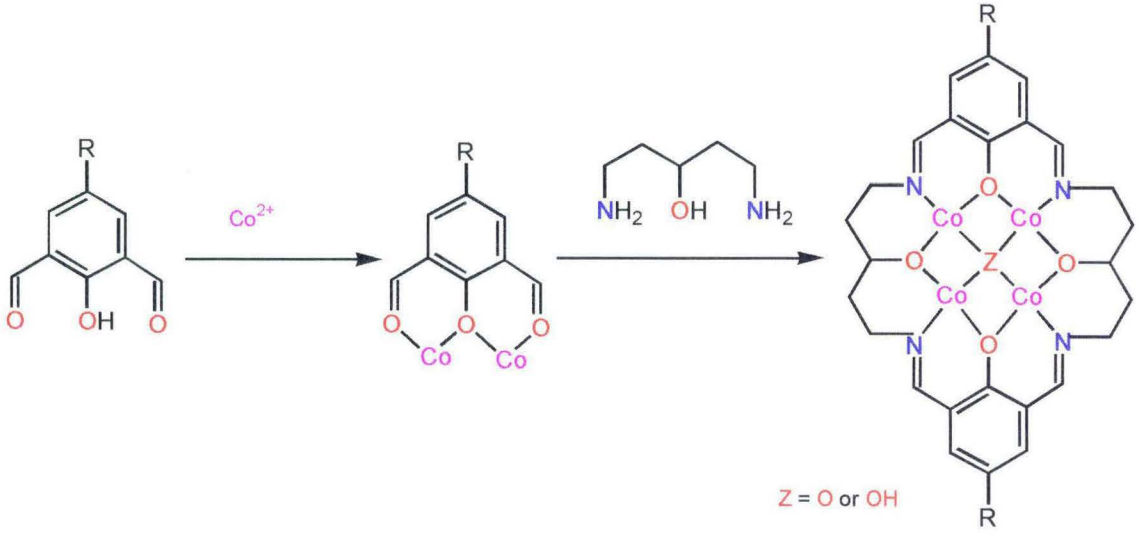


Figure 4·1 : Formation of the Tetranuclear Cobalt complexes

All of these reactions were carried out with and without the presence of triethylamine (TEA). It was expected the TEA would enhance the

formation of tetranuclear products. Initially the cobalt syntheses were carried out in the manner previously described for the copper complexes (Chapter 3). However, the yields were poor and often the first products (pinkish-brown powders) were shown by IR to be, not macrocyclic complexes, but inorganic cobalt salts or mixtures. For this reason, almost all of the reactions were repeated with the length of time of the reflux period increased from the usual 24 h to greater than 60 h and under these conditions macrocyclic products were obtained.

3 : THE ACETATE COMPLEXES

3·I : Acetate Complexes with LV5

Only tetranuclear products have been characterised when cobalt acetate salts are used with the **LV5** and **LV5t** ligand systems. The presence of the acetate ions affects the pH of the reaction mixture, enhancing deprotonation of the alcohol and phenol groups and this seems to favour the formation of four-centred products. Also, the acetate ion can be described as having the right "bite" to bridge two metal centres completing the coordination spheres of the metals and reducing the net charge and thus the solubility of the complexes. This also appears to encourage the isolation of tetranuclear products. In all cases the first products from these reactions were inorganic salts and often macrocyclic products were only recovered after additional treatment of the reaction mixtures in some way. These treatments included the addition of LiCl, NH_4NCS and NaN_3.

Crystals of complex **8** $[Co_4(\mu_4\text{-}O)\mathbf{LV5}(CH_3COO)_4]Cl\cdot 3H_2O$ were obtained from the very last reaction tried in this series. Although this reaction was set up in the same way as those done previously (see Experimental), it proceeded differently. Firstly, it was observed that when the cobalt acetate was initially dissolved in the MeOH, a brilliant purple solution formed. In all previous reactions the reaction mixture was a golden colour at this point. Once all the other components had been added the reaction solution became deep brown. Secondly, as after 67 h of refluxing no solid was evident (previous reactions

contained brown solids at this point), the mixture was taken down to dryness under vacuum and CH_3CN added. This had previously been shown[221] to be a good way to remove any KCl which may be present. Analysis of the undissolved khaki powder filtered from this mixture showed it to be a combination of a macrocyclic compound and inorganic cobalt salts. Because it was very late at night in a very cold laboratory, instead of treating the reaction mixture further, the entire filtered solution was set up for vapour diffusion of ether. Large black-brown crystals formed in this filtrate and were suitable for X-ray crystal structure analysis.* The initial refinement revealed a macrocyclic complex containing four cobalt ions with four acetate groups coordinated to these cobalts (Fig. 4·2).

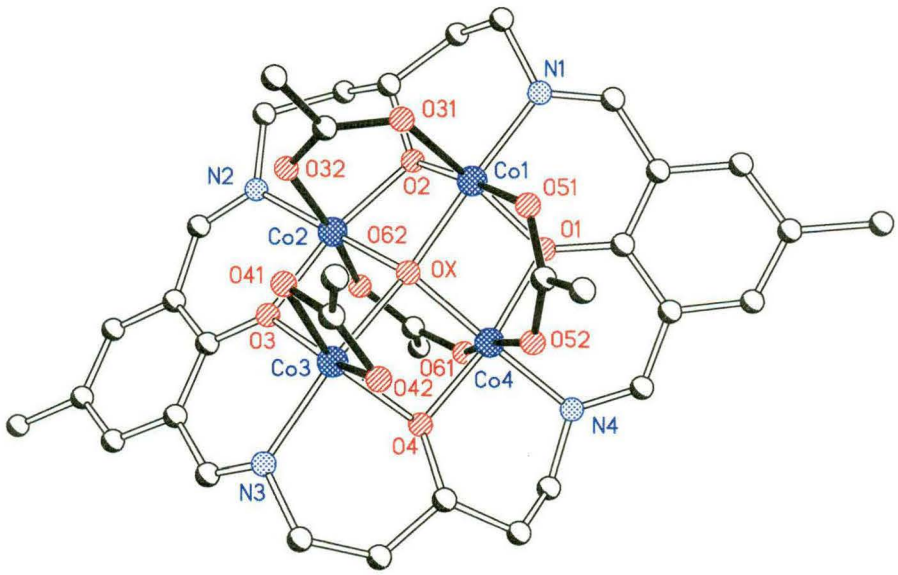


Figure 4·2 : The cation of complex 8 - $[Co_4(\mu_4\text{·}O)LV5(CH_3COO)_4]\text{·}Cl\text{·}3H_2O$

Unlike the previously reported copper complexes of **LV5** this macrocycle is not planar. The four cobalt ions are bound within the **LV5** macrocycle with each being coordinated to one imine nitrogen, one phenoxide oxygen, one alkoxide oxygen and the central oxo (Ox) ion. The coordination spheres of the cobalt ions are completed by acetate ligands. Three acetate ions are bound to one "face" of the macrocycle. The first two link Co1 to Co2 and to Co4 respectively,

* The data were collected on the second to last day in Belfast and the diffractometer developed a fault before the desired amount of data had been collected. By departure time for New Zealand the refinement had progressed to the point of identifying the macrocycle containing four cobalt ions and four acetate groups coordinated to these cobalts. Unfortunately the crystals were misplaced in the move so no recollection has yet been possible.

and the third is bound as a bidentate ligand to Co3. The fourth acetate bridges Co2 and Co4 across the centre of the macrocycle on the opposite "face" to the other three. This bridge may be responsible for the considerable twist (Fig. 4·3) exhibited by this macrocycle. There is a dihedral angle of 44·6° between the planes defined by the phenol rings with respect to each other. The Co····Co distances [Co1····Co2 - 2·809(2), Co2····Co3 - 3·030(1), Co3····Co4 - 2·978(2), Co4····Co1 - 2·806(2) Å] are short but not bonding. It is worth noting that the bond lengths from the cobalt ions to the central oxygen (Ox) are not significantly different to those between cobalt and the macrocyclic donors implying that these bonds are all of comparable strength. This is in contrast to the tetranuclear copper complexes where the copper to Ox bonds are longer than to other donors. The geometry at the μ_4-Ox is now approximately tetrahedral which is much more common than the square pyramidal geometry seen in the copper complexes.

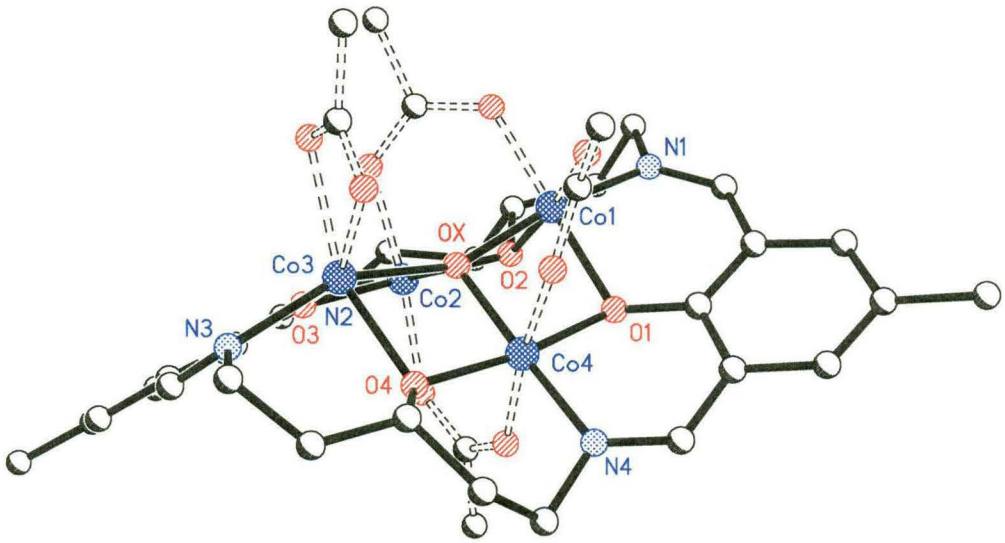


Figure 4·3 : Complex 8 showing the 44·6° twist of the two phenol rings with respect to each other.

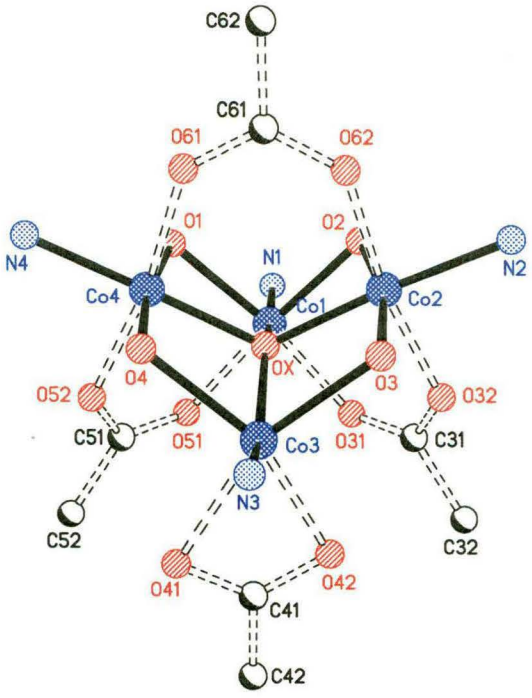


Figure 4·4 : Showing the "butterfly" arrangement of the central core of complex 8

Co1, Co2 and Co3 have approximate octahedral coordination while Co4 is distorted square pyramidal (Fig. 4·4). The central core of the macrocycle has a "butterfly" arrangement with an angle of 126·4° being found between Co4····Ox····Co2. M^{c}Kee[47] has previously reported this arrangement in a tetranuclear mixed valence manganese complex of **LV5** where an Mn2····Ox····Mn4 angle of 141·9° is seen.

The coordination geometry and examination of the bond lengths around the four cobalt ions suggested that three of these were Co(III) and one was Co(II). This assignment is supported by a comparison with other characterised compounds. In his investigation of the mixed valence cobalt complexes of **L3-3**[*] Robson commented on a general contraction of the bond lengths of the N_2O_2 donor associated with Co(III) over those associated with Co(II) ions.[100] The Co(III) bond lengths are shorter because of the higher charge on the metal ion and the consequently stronger electrostatic interactions with the donor groups. The Co(III) ion is smaller than its Co(II) counterpart because it is d^6 as compared to d^7 and it is low spin. Table 4·1 shows the Co to coordinating atom

[*] This study has been discussed fully in Chapter 1 pp 27-30.

bond lengths for complex **8** and the two previously characterised cobalt complexes **M15** and **M16** prepared by M^{c}Kee[157]. The Co(III) ions, as would be expected, are clearly identified as having considerably shorter bond lengths than their Co(II) counterparts. Careful consideration must be taken when using bond lengths as an indication of oxidation state. Bond lengths will also be dependent on spin state so even for Co(III) there can still be significant variation in bond length depending on high or low spin. Another consideration is that with chelating ligands (including macrocycles) the bond length is as much a function of the ligand geometry constraints as it is the nature of the metal ion. The use of bond lengths in the following assignment of the oxidation states is considered valid in this case as macrocyclic donors are the same in all three cases.

Table 4·1 : Cobalt to nearest neighbour distances for Complexes 8, M15, and M16 (The Co(II) bond lengths are shown in colour.)

Complex 8 [$Co^{II}Co^{III}_3(\mu_4$-O)LV5$(CH_3COO)_4$]

	phenolate	oxo	alkoxide	imine	acetate	chloride
Co1	1·89	1·93	1·90	1·93	1·88 1·90	
Co2	1·91	1·91	1·90	1·94	1·89 1·90	
Co3	2·14	2·03	2·03	2·03	2·13 2·21	
Co4	1·89	1·92	1·90	1·90	1·88 1·91	

Complex M15 [Co^{II}_4LV5$(CH_3COO)_2Cl_2$]

Co1	2.11		1·98	2·02	2·10 2·06	
Co2	1·97		1·96	2·03	2·26	2·28

Complex M16 [$Co^{III}_3Co^{II}(\mu_4$-O)LV5$(CH_3COO)_3Cl]\cdot ClO_4$

Co1	2·13	2·00	1·98	2·01	2·01	2·27
Co2	1·89	1·92	1·89	1·90	1·90 1·90	
Co3	1·90	1·93	1·90	1·94	1·93 1·87	
Co4	1·87	1·90	1·89	1·93	1·90 1·91	

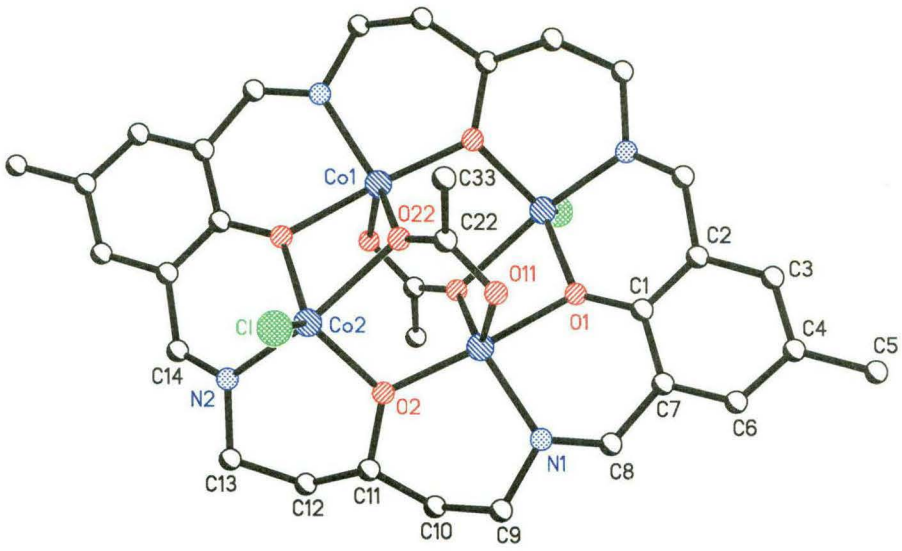


Figure 4·5 : Complex M15 [Co^{II}_4LV5$(CH_3COO)_2Cl_2$]

In complex **M15** [Co^{II}_4**LV5**$(CH_3COO)_2Cl_2$] (Fig. 4·5) both of the alcohol and phenol groups are deprotonated and each bridges two cobalt ions. The macrocycle is approximately planar with two acetate ions bridging the macrocycle on opposite faces and each acetate ion coordinated to three cobalt ions. The complex has a centre of symmetry. Both cobalt ions in the asymmetric unit are five coordinate and the coordination geometry is approximately trigonal bipyramidal (Fig. 4·6).

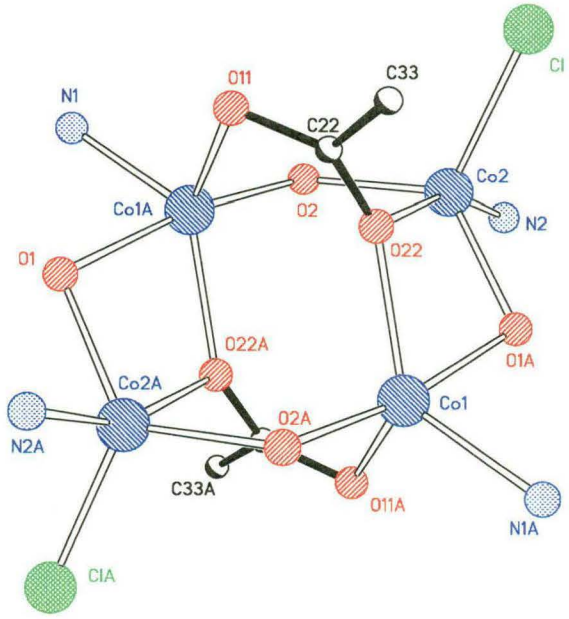


Figure 4·6 : The central core of Complex M15

Co1 is coordinated to O1a, N1a, and O2a of the macrocycle, O11a of one and O22 of a second bridging acetate. The O22 of the acetate is also bonded to the Co2 and it is this bidentate coordination that distorts the geometry away from planarity around the cobalt. Co2 is coordinated to O1a, N2, and O2 of the ligand and to O22. The fifth axial position is occupied by a chloride ion. As no other anions are were found in the structure the charge balance is satisfied if all the cobalt ions are Co(II) and this is supported by the coordination geometry. All of the cobalt ions are square pyramidal. Notably, this is the only tetranuclear complex, in this series, which does not contain a central donor ion.

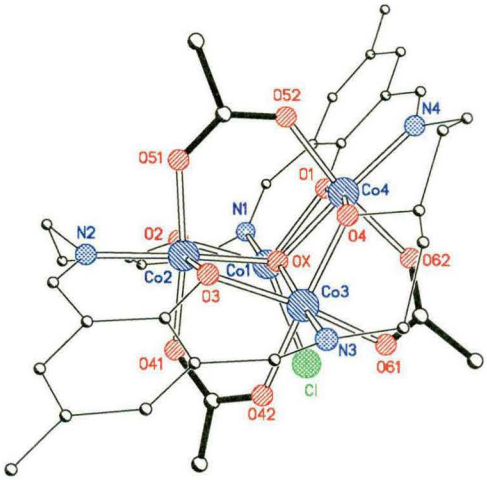


Figure 4·7 : The cation of Complex S2 - $[Co^{III}_3Co^{II}(\mu O)LV5(CH_3COO)_3Cl]\cdot ClO_4$

As with the previous two complexes, in complex **M16** the alcohol and phenol groups are deprotonated and bridge the cobalt ions. Co1 (Fig. 4·7) exhibits square pyramidal geometry with the four positions of the basal plane being occupied by O1, N1, and O2 of the macrocycle along with the central oxo (Ox) ligand which is bound to all four cobalts. Co2, Co3, and Co4 have octahedral geometry. As in **8** the macrocycle is twisted with the phenol rings being at an angle of 42·6° to each other. This complex also has a butterfly arrangement to the core (Fig. 7) with the Co2····Ox····Co4 being 54·8°. A perchlorate anion is found in the lattice and so the charges balance if the complex is $Co^{III}_3Co^{II}$. Co2, Co3 and Co4 are designated Co(III) and Co1 is Co(II) with this assignment being supported by the coordination geometries and the bond lengths around these ions (Table 4·1).

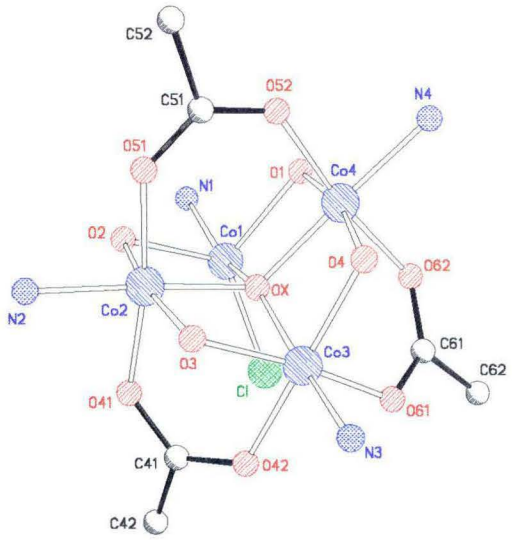


Figure 4·9 : The core of Complex M16

Having established with reasonable certainty that the cobalt ions in complex **8** must be three Co(III) and one Co(II) and with the structure having three acetates, one chloride and a μ-oxo, charge balance required one further anion. It was most likely that this would be a chloride ion as it had been found almost impossible to exclude chloride ions, released from the dihydrochloride salt of the amine, from these reaction mixtures. If this were the case then the chloride ion would have been expected to be seen in the electron density map early on in the structure solution. The other possibility was a free OH^- ion from water but a literature search showed no precedents for this with such weak amines. Examination of the packing diagram, at this point of the refinement, showed that the macrocycles were arranged in layers with all the residual electron density lying in between these layers. There was hydrogen bonding evident between this layer and the macrocycles as well as within the layer. The structure was modelled to contain a chloride ion which had quarter occupancy of four alternative positions (Fig. 4·8) and the refinement then converged. Subsequent to proposing this model the missing crystals arrived. Unfortunately they had deteriorated so that another data set could not be collected but chemical analysis* of them suggests that the model was indeed correct.

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* Analysing for $[Co_4(\mu_4\text{·}O)\mathbf{LV5}(CH_3COO)_4]\text{·}Cl\text{·}3H_2O$; Calculated C: 40·56; H: 4·73; N: 5·26 % Found C: 40·68; H: 4·78; N: 5·25 %.

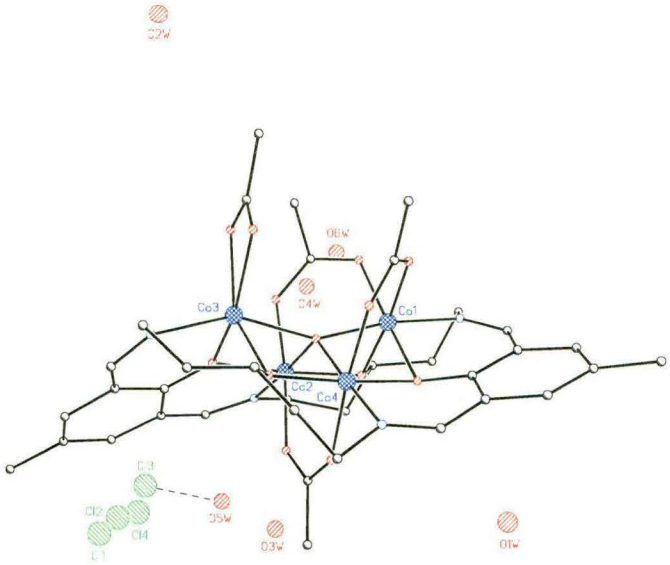

Figure 4·9 : Showing the alternate positions of the quarter occupancy chloride ions and the water molecules in the structure. O1w is a full occupancy water while the other five (O2w, O3w, O4w, O5w, and O6w) are all half occupancy

In the crystal the macrocycles are arranged in layers which are connected through an interesting hydrogen-bond network based around the chloride ion sites (Fig. 4·11). Details of this network are shown in Figure 4·10. As expected, the hydrogen bond distances to the chloride ions are longer than the $H_2O\cdots H_2O$ interactions, supporting the model used. One of the oxygens (O41) of the bidentate acetate is hydrogen-bonded to a water molecule (O1w) which in turn is bonded to Cl1. The chloride is bound to three other water molecules O5w, O2w, and O4w. The network then extends from O5w to O3w and so to O2wa which is bound through the same system to O41a in a second macrocycle in the next layer. The macrocycles are disposed in alternating directions in neighbouring layers.

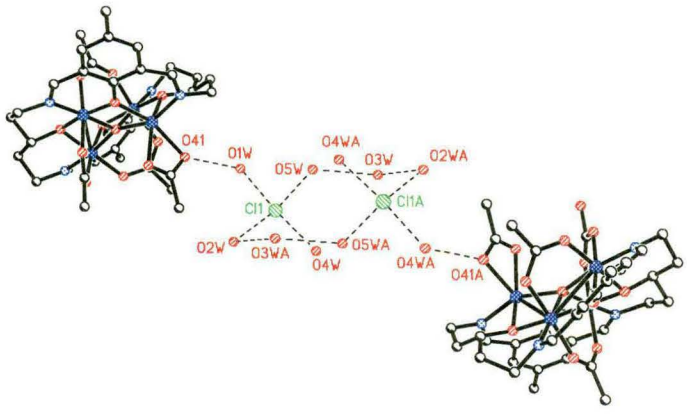

Figure 4·10 : Showing detail of the hydrogen bonding

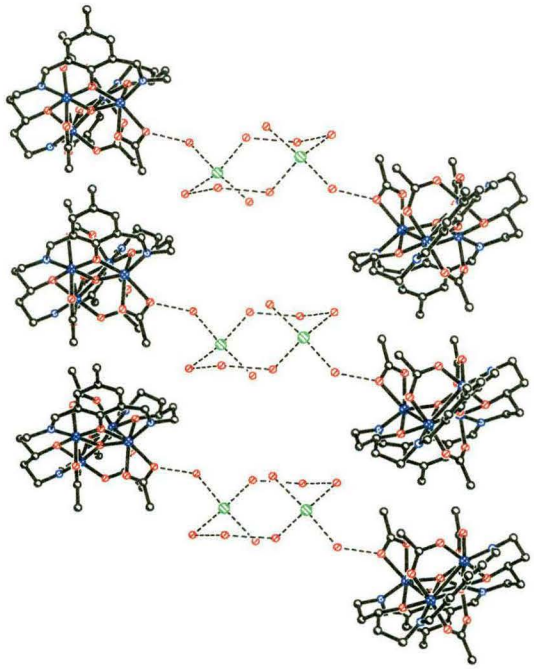

Figure 4·11

Table 4·2 : Selected bond lengths [Å] for 8 $[Co_4(\mu_4\text{·}O)LV5(CH_3COO)_4]\text{·}Cl\text{·}3H_2O$

Co1-O31	1·884(6)	Co1-OX	1·886(5)	Co1-O51	1·902(5)
Co1-O2	1·903(5)	Co1-N1	1·925(6)	Co1-O1	1·935(5)
Co1-Co4	2·806(2)	Co1-Co2	2·809(2)	Co2-O62	1·890(6)
Co2-O32	1·896(6)	Co2-O2	1·904(5)	Co2-O3	1·905(5)
Co2-OX	1·905(5)	Co2-N2	1·937(7)	Co3-O4	2·026(5)
Co3-O3	2·031(5)	Co3-N3	2·041(7)	Co3-O42	2·136(6)
Co3-OX	2·137(5)	Co3-O41	2·207(6)	Co3-Co4	2·978(2)
Co4-O4	1·881(5)	Co4-O61	1·887(6)	Co4-OX	1·892(5)
Co4-N4	1·894(6)	Co4-O52	1·911(6)	Co4-O1	1·919(5)
O1-C1	1·360(9)	O2-C11	1·446(9)		

Table 4·3 : Selected bond angles [°] for 8 $[Co_4(\mu_4\text{·}O)LV5(CH_3COO)_4]\text{·}Cl\text{·}3H_2O$

O31-Co1-OX	94·2(2)	O31-Co1-O51	84·7(2)	OX-Co1-O51	94·2(2)
O31-Co1-O2	92·0(2)	OX-Co1-O2	82·3(2)	O51-Co1-O2	175·0(2)
O31-Co1-N1	92·8(3)	OX-Co1-N1	170·9(3)	O51-Co1-N1	92·3(3)
O2-Co1-N1	91·7(3)	O31-Co1-O1	172·4(2)	OX-Co1-O1	83·3(2)
O51-Co1-O1	88·3(2)	O2-Co1-O1	94·8(2)	N1-Co1-O1	90·4(3)
O62-Co2-O32	169·8(2)	O62-Co2-O2	90·6(2)	OX-Co2-N2	176·2(3)
O32-Co2-O2	93·3(2)	O62-Co2-O3	90·4(2)	O32-Co2-O3	88·0(2)
O2-Co2-O3	166·8(2)	O62-Co2-OX	99·8(2)	O32-Co2-OX	90·2(2)
O2-Co2-OX	81·8(2)	O3-Co2-OX	85·1(2)	O62-Co2-N2	84·0(3)
O32-Co2-N2	86·1(3)	O2-Co2-N2	99·2(3)	O3-Co2-N2	94·0(3)
Co2-OX-Co3	97·0(2)	O4-Co4-O61	91·1(2)	O4-Co4-OX	86·8(2)
N2-Co2-Co1	137·7(2)	O4-Co3-O3	106·4(2)	O4-Co3-N3	86·5(2)

O3-Co3-N3	88·9(2)	O4-Co3-O42	152·4(2)	O3-Co3-O42	96·7(2)
N3-Co3-O42	109·2(2)	O4-Co3-OX	77·0(2)	O3-Co3-OX	76·3(2)
N3-Co3-OX	153·4(3)	O42-Co3-OX	94·6(2)	O4-Co3-O41	96·1(2)
O3-Co3-O41	156·9(2)	N3-Co3-O41	97·9(3)	O42-Co3-O41	60·2(2)
OX-Co3-O41	104·3(2)	Co1-OX-Co2	95·6(2)	Co4-OX-Co2	126·4(3)
O61-Co4-OX	99·2(2)	O4-Co4-N4	94·3(3)	O61-Co4-N4	82·6(3)
OX-Co4-N4	177·9(3)	O4-Co4-O52	89·8(2)	O61-Co4-O52	170·6(2)
OX-Co4-O52	90·2(2)	N4-Co4-O52	88·0(3)	O4-Co4-O1	170·3(2)
O61-Co4-O1	89·6(2)	OX-Co4-O1	83·6(2)	N4-Co4-O1	95·4(3)
O52-Co4-O1	91·2(2)	Co1-OX-Co3	153·5(3)	Co1-OX-Co4	95·9(2)
Co4-OX-Co3	95·1(2)	Co4-O1-Co1	93·5(2)	Co1-O2-Co2	95·1(2)
Co2-O3-Co3	100·6(2)	Co4-O4-Co3	99·3(2)		

As mentioned, crystals of complex **8** were isolated from the very last reaction in the series of preparations using cobalt acetate. Complexes isolated from earlier syntheses in this series have been identified by "sporting techniques". Four cobalt acetate complexes of **LV5** have been identified and these are shown in Table 4·4.

Table 4·4 : Complexes with Acetate

8	$[Co_4(\mu_4\text{-}O)\mathbf{LV5}(CH_3COO)_4]\cdot Cl\cdot 3H_2O$
9	$[Co_4(\mu_4\text{-}O)\mathbf{LV5}(CH_3COO)_4]\cdot Cl\cdot 3H_2O\cdot CH_3CH_2OH$
10	$[Co_4(\mu_4\text{-}O)\mathbf{LV5}Cl(CH_3COO)_3]\cdot[CoCl_4^{2-}]\cdot CH_3OH\cdot 4H_2O$
11	$[Co_4\mathbf{LV5}Cl_4(CH_3COO)_3]$

A brown powder, complex **9**, was isolated from the filtrate of **8**. The IR spectra (Table 4·5) of **8** and **9** are almost exactly the same and a similar fragmentation pattern is seen in their FAB-ms spectra. Chemical analysis supports the identity of **9** as $[Co_4(\mu_4\text{-}O)\mathbf{LV5}(CH_3COO)_4]\cdot Cl\cdot 3H_2O\cdot CH_3CH_2OH$ which differs from the crystals only in that it includes an ethanol solvent molecule.

Table 4·5 : Selected IR frequencies (cm^{-1}) for the cobalt acetate complexes

8	2907	2858	1642		1386		963	925	889	821	
9	2922	2864	1638		1384		962	920	887	820	
10	2924	2860	1641			1316	960		887	820	761
11	3006	2853	1642	1628	1349	1326	965		891	816	772

In the first preparation in this series, the reaction mixture was a deep red solution which yielded no solid after refluxing for 24 h and sitting for six days.

Two products were collected after the addition of LiCl to this solution and both of these were identified as tetranuclear complexes. The first compound was collected as a very fine brown powder and the second as a deep olive green microcrystalline solid. The base peaks in the FAB-ms identify the macrocyclic cations as $[Co_4(\mu_4\text{-}O)\mathbf{LV5}(CH_3COO)_4]^+$ and $[Co_4(\mu_4\text{-}O)\mathbf{LV5}Cl\ (CH_3COO)_3]^+$ respectively (Table 4·6). Although the cation of the brown powder can be identified the product appears to be a mixture and no formula has been assigned. The second product (complex **10**) has been speculatively assigned the formula $[Co_4(\mu_4\text{-}O)\mathbf{LV5}Cl(CH_3COO)_3]\cdot CoCl_4^{2-}\cdot CH_3OH\cdot 4H_2O$ which contains the above cation, closely matches the chemical analysis and is supported by the colour of the complex. The green colour in many, but not all, of the complexes is attributed to the presence of the $CoCl_4^{2-}$ anion. This anion was found in the crystal structure of one of the binuclear complexes which will be discussed in the following chapter. However, this formulation infers that complex **10** contains four Co(III) ions and although this fills one of the gaps in the series of complexes that was one of the stated aims of this project, it is uncertain if this assignment can be justified. With four Co(III) ions the complex could indeed be planar and octahedral coordination around the metal ions could be achieved with water molecules completing the coordination spheres. This proposal then leads to speculation as to the manner of coordination of the acetate groups. Recently, the tetranuclear nickel complex of **LV5t** (**M17**), in which acetic acid groups are found bound to the copper ions in the manner shown in Figure 4·12, has been reported[222].

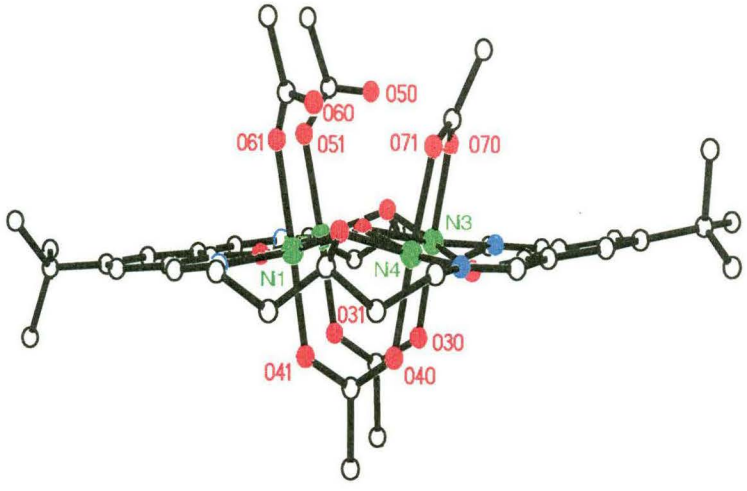

Figure 4·12 : The cation $[Ni_4LV5t(CH_3COO)_3(CH_3COOH)_2]^{3+}$ of M17 showing two coordinated acetic acid groups

Differences in the IR of complex **10** suggest that its structure varies from that in complexes **8** and **9** and it is also possible that one (or more) acetate groups may be acetic acid groups in which case not all four cobalts would be in the +3 oxidation state. All three show similar fragmentation patterns in the FAB-ms spectrum, all three products show sequential loss of acetate ions.

The second time this synthesis was tried a brown solid (complex **11**) appeared within a very short time. It was tempting to identify **11** as $[Co_4(\mu_4\text{-}O)\mathbf{LV5}(CH_3COO)_2]$ $[CoCl_4^{2-}]$ as this formula appeared to be supported by ions in the FAB-ms, but the chemical analysis did not agree. It would also be expected that if the $CoCl_4^{2-}$ anion was present then the colour of **11** would be green. Alternative explanations for ions found in the ms supported interpreting the chemical analysis results as $[Co_4\mathbf{LV5}Cl_4(CH_3COO)_3]$. This product is quite clearly different from the others. The IR spectra for the first three contain a large broad peak at ~3400 due to H_2O and this is quite small in **11**. Other differences are that both the imine and the acetate peaks are split (Table 4·5).

Table 4·6 : Selected FAB-ms ions of the LV5 - acetate complexes

		8	**9**	**10**	**11**
$Co_4\mathbf{LV5}O(OAc)_2\,CoCl_4\,H_2O$	1075				1074
$Co_4\mathbf{LV5}Cl_4(OAc)_3Cl$	1076				
$Co_4\mathbf{LV5}O(OAc)\,CoCl_4\,H_2O$	1016				1016
$Co_4\mathbf{LV5}Cl_4(OAc)_2Cl$	1016				
$Co_4\mathbf{LV5}O(OAc)_4Cl$	995		994		
$Co_4\mathbf{LV5}O(OAc)_4$	976	976	976		980
$Co_4\mathbf{LV5}O(OAc)_3Cl$	952		952	952	
$Co_4\mathbf{LV5}O(OAc)_3$	917	917	917		
$Co_4\mathbf{LV5}O(OAC)Cl_3$	904				906
$Co_4\mathbf{LV5}O(OAc)Cl_2$	869				867
$Co_4\mathbf{LV5}O(OAc)_2$	858	858	858	858	
$Co_3\mathbf{LV5}O(OAc)_3$					
$Co_4\mathbf{LV5}O(OAc)$	799	797	799	796	
$Co_3\mathbf{LV5}O(OAc)_2$					
$Co_4\mathbf{LV5}O$	740	740	738	738	738
$Co_3\mathbf{LV5}O(OAc)$					

3·2 : LV5 - Acetate Complexes treated with Thiocyanate or Azide

A number of the earlier **LV5** - acetate reaction mixtures were treated with either azide or thiocyanate. In the absence of any crystal structures of these products the assignment of formulae has been extremely difficult. The similarity of the accurate masses of cobalt (58·933197), CH_3COO^- (59·013304) and NCS^- (57·975145) has meant that FAB-ms has not always been very helpful and must be used in combination with careful examination of the IRs for NCS and OAc peaks. Even in conjunction with the chemical analysis it has not always been possible to assign formulae with any degree of certainty. Table 4·7 illustrates this point.

Table 4·7 : Comparison of accurate mass and C,H,N analysis for a variety of Co - OAc - NCS - LV5 complexes

Formula	Accurate mass	C, H, N Analysis		
		C	H	N
Co_4**LV5**$OH(NCS)_6(CH_3COO)H$	1148·849490	37·6	3·2	12·2
Co_3**LV5**$OH(NCS)_6(CH_3COO)_2H$	1148·929997	39·7	3·5	12·2
Co_4**LV5**$OH(NCS)_5(CH_3COO)_2$	1148·880224	38·7	3·4	11·0
Co_3**LV5**$OH(NCS)_5(CH_3COO)_3$	1148·960331	40·7	3·7	11·0
Co_3**LV5**$OH(NCS)_6(CH_3COO)_2$	1147·922172	39·7	3·4	12·2
Co_3**LV5**$OH(NCS)_4(CH_3COO)_4$	1149·998489	41·8	3·9	9·7
Co_4**LV5**$OH(NCS)_4(CH_3COO)_3$	1149·918383	39·7	3·7	9·7
Co_4**LV5**$OH(NCS)_3(CH_3COO)_4$	1150·956541	40·7	3·9	8·5
Co_2**LV5**$H_2O(NCS)_6(CH_3COO)_3$	1149·010104	41·8	3·8	12·2
Co_2**LV5**$OH(NCS)_5(CH_3COO)_4$	1149·040437	42·8	3·9	11·0
Co_2**LV5**$OH(NCS)_4(CH_3COO)_5$	1150·078596	43·8	4·2	9·7

The correct formula may be able to be determined by high resolution mass spectrometry, but this is also difficult when the mass is as big as in these complexes. Another possibility is electrospray mass spectrometry in conjunction with a suitable isotope ratio programme and it is expected that both these techniques will be tried in the future.

The products for which formulae have been assigned are listed in Table 4·8.

Table 4·8 : Complexes from LV5 - OAc - NCS or N_3 mixtures

12	$Co_4(\mu_4\text{-}O)$**LV5**$(NCS)_4(CH_3COO)(CH_3CH_2OH)_{1.5}(H_2O)_2$
13	Co_4**LV5**$(NCS)_4)(CH_3CH_2OH)$
14	$Co_4(\mu_4\text{-}O)$**LV5**$(NCS)_4)(NH_4NCS)(CH_3CH_2OH)$
15	Co_4**LV5**$(N_3)_4Cl(CH_3COO)_2$

In the first reaction, double the usual amount of the reactants was used and the procedure carried out in a N_2 atmosphere. As the first products of this reaction were not macrocyclic, the filtrate was treated with an excess of NH_4NCS and a significant amount of bright green powder and subsequently another deep green solid were then collected. Analysis, IR, and FAB-ms of the first of these products (complex **12**) shows it to be tetranuclear and it has been assigned as $Co_4(\mu_4\text{-}O)$**LV5**$(NCS)_4(CH_3OH)_4$. The base peak in the FAB-ms appears to be for four cobalts with an oxygen and four thiocyanate molecules (Table 4·9). The second product contains the same nucleus but the rest of the structure cannot be assigned.

Table 4·9 : Selected ions (FAB-ms) for Co - OAc - NCS complexes

		12	**13**	**14**
Co_4**LV5**$(OH)(NCS)_6(CH_3COO)H$ Co_3**LV5**$(OH)(NCS)_6(CH_3COO)_2H$	1149			
Co_4**LV5**$(NCS)_4(CH_3COO)_2(H_2O)$	1092			1093
Co_4**LV5**$(O)(NCS)_4(CH_3COO)(H_2O)$	1049			1036
Co_4**LV5**$(NCS)_4(H_2O)H$	975	975	975	975
Co_4**LV5**$(NCS)_3(H_2O)H$	916	917	917	918
Co_4**LV5**$(NCS)_2(H_2O)$	858	858	858	859
Co_4**LV5**$(NCS)OH$	799	799	799	799
Co_4**LV5**(O)	740	738		

The filtrate of another cobalt acetate reaction was refluxed for some time with NH_4NCS and three products were subsequently isolated. The IRs were all similar and the 975·1 ion for $[Co_4(\mu_4\text{-}OH)$**LV5**$(NCS)_4]$ is in the FAB-ms of all of them. For the second two it is also the base peak. Chemical analysis of the first product shows it to be a mixture of complexes of both the full and an open-

sided ligand and this is backed up by a significant peak (in the ms) being seen for the open-sided ligand. This open-sided complex is discussed more fully in Chapter 5. The second product (complex **13**) is assigned the formula $Co_4(\mu_4$-OH)**LV5**$(NCS)_4)(CH_3CH_2OH)$ and for the third (complex **14**), which appears to have some NH_4NCS incorporated into its structure, the proposed formula is $Co_4(\mu_4$-OH)**LV5**$(NCS)_4)(NH_4NCS)CH_3CH_2OH$. A tiny peak for the latter is found in its mass spectrum.

Treatment of another cobalt acetate - **LV5** reaction mix with NaN_3 gave complex **15** which has been assigned the formula Co_4**LV5**$(N_3)_4Cl(CH_3COO)_2$. This formulation is supported by fragments seen in the FAB-ms and the microanalysis results.

3·3 : Acetate Complexes with LV5t

No complexes of the *t*-butyl ligand with just cobalt acetate were isolated, but subsequent treatment of these reaction mixtures with either NCS or N_3 yielded the products identified in Table 4·10.

Table 4·10 : Co - OAc - NCS or N_3 complexes of LV5t

16	$Co_4(\mu_4$-O)**LV5t**$(NCS)_4)(CH_3COO)\cdot CH_3OH$
17	$Co_4(\mu_4$-O)**LV5t**$(N_3)_4(CH_3COO)_2$
18	$Co_4(\mu_4$-O)**LV5t**$(N_3)_{4.5}(Cl_{2.5})(H_2O)_2CH_3OH$

When half of a filtered dark brown cobalt acetate reaction mixture was treated with NH_4NCS the colour changed to deep green. Complex **16**, which has been assigned the formula $Co_4(\mu_4$-O)**LV5t**$(NCS)_4(CH_3COO)\cdot CH_3OH$, was isolated as a green brown powder. This assignment is supported by ions in the FAB-ms (Table 4·11) and the chemical analysis.

Table 4·11 : Selected ions (FAB-ms) for complex 16

Co_4**LV5t**$(NCS)_4(H_2O)H$	1059
Co_4**LV5t**$(NCS)_3(H_2O)H$	1001
Co_4**LV5t**$(NCS)_2(H_2O)H$	942

Treatment of the other half of the filtrate of the same reaction mixture with NaN_3, initially yielded quite large amounts of buff coloured powders which IR and analysis showed to be predominantly inorganic salts. A small amount of $Co_4(\mu_4\text{-}OH)$**LV5t**$(N_3)_4(CH_3COO)_2$ (complex **17**) and $Co_4(\mu_4\text{-}OH)$**LV5t**$(N_3)_{4.5}(Cl_{2.5})(H_2O)_2CH_3OH$ (complex **18**) were later isolated as olive green powders. Because of the difficulty of safe disposal of cobalt azides the rest of this reaction mixture was discarded and the reaction was not tried again.

4 : THE PERCHLORATE COMPLEXES

One tetranuclear complex has been identified when the perchlorate anion was used. A series of syntheses, using only two metal equivalents, had been carried out. It was hoped that binuclear products would result. Interestingly, the first tetranuclear complex isolated from reactions between **LV5** and cobalt perchlorate came from one of these syntheses. This greenish-brown powder has been identified, by analysis, as **19** Co_4**LV5**$Cl_3(ClO_4)(CH_3CH_2OH)_2{\cdot}H_2O$ with the [Co_4**LV5**$Cl_3(ClO_4)$] fragment being seen in the FAB-ms. It is interesting to speculate as to why a tetranuclear product resulted from this particular reaction. It may be that the tetranuclear complex has greater thermodynamic stability and lower solubility than the binuclear complexes. If there is a dynamic equilibrium between the two, then as the tetranuclear product precipitates out, more is formed. If this is so, it indicates that the relative solubility is important. It appears that the aim of forming a tetranuclear cobalt macrocyclic complex with counterions other than acetate has been achieved and that in this complex all the cobalt ions are Co(II).

5 : THE CHLORIDE COMPLEXES

The syntheses using cobalt chloride yielded quite a number of tetranuclear products with both **LV5** and **LV5t**; the **LV5** ligand also formed binuclear complexes which will be discussed in the next chapter.

5·1 : Chloride complexes with LV5

Table 4·12 : Chloride complexes with LV5

20	$Co_4(\mu_4\text{-}O)$**LV5**$Cl_4(CH_3OH)H_2O$
21	$[Co_4$**LV5**$Cl_4]_2$·dahp·$4H_2O$·$2CH_3OH$

The first of these came from a reaction mixture in which a brownish solid formed around the solvent line within a very short time of refluxing beginning. After 22 h significant amounts of two products were noticeable in this mixture. The first was a fine green powder and the second was a dark green crusty material which was sticking to the flask around the solvent line and which had a "polymeric" look to it. Because of the differences in appearance these products were separated manually and collected. The IRs of both of these were identical and all the major peaks in the FAB-ms were also the same but the analyses of these two were somewhat different. The fine powder (complex **20**) has been assigned the formula $Co_4(\mu_4\text{-}O)$**LV5**$Cl_4(CH_3OH)H_2O$ which agrees extremely well with the analysis and is supported by the FAB-ms and IR. This assignment means that the complex contains two Co(II) and two Co(III) ions and the formation of such a complex was one of the stated aims of this project.

Table 4·13 :
Selected ions (FAB-ms) for Co -LV5 - Cl complexes

		20	**21**
Co_4**LV5**Cl_4dahpOH			995
Co_4**LV5**Cl_6OH	951	951	951
Co_4**LV5**Cl_4OH	883	887	887
Co_3**LV5**Cl_4OH	822	822	815
Co_3(H**LV5**)Cl	785	789	787
Co_2**LV5**Cl_4	750	750	750
$Co_2(H_2$**LV5**$)Cl_4$	713	715	715
$Co(H_2$**LV5**$)Cl_4$	689	689	689
Co**LV5**Cl_3H	653	653	653

The "polymeric" product (complex **21**) has been assigned as a dimer of two $[Co_4\mathbf{LV5}Cl_4]$ units linked by a dahp unit i.e. $[Co_4\mathbf{LV5}Cl_4]_2{\cdot}dahp{\cdot}4H_2O{\cdot}2CH_3OH$. This formulation matches the analysis and an ion for one of these units with a dahp fragment is seen in the ms. It is speculated that the two macrocyclic units could be folded in the manner already seen for the copper complex (Complex **7**, p 121) and linked by the dahp fragment (Fig. 4·13).

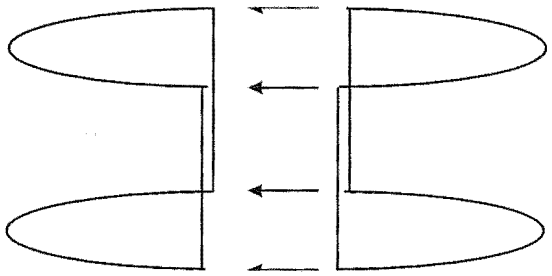

Figure 4·13

Because, at Belfast, FAB-ms and electron impact (EI) ms were available both were run for many of these complexes. It was particularly hoped that electrospray ms might be able to show the parent ion of these complexes. It was decided that more information was gained from the FAB-ms.

5·2 : Chloride complexes with LV5t

Table 4·14 : Chloride complexes with LV5t

22	$Co_4\mathbf{LV5t}Cl_5(CH_3OH)(H_2O)_2$
23	$Co_4\mathbf{LV5t}Cl_4(H_2O)_5$
24	$Co_4\mathbf{LV5t}Cl_5(H_2O)_{1.5}$

When the *t*-butyl phenol was used in the chloride syntheses only tetranuclear products were isolated. Two products were isolated, in good yield, from the first reaction mixture. The first, a deep moss green powder (Complex **22**), came directly from the cooled reaction mixture and has been assigned the formula $Co_4\mathbf{LV5t}Cl_5(CH_3OH)(H_2O)_2$. The second, complex **23**, formulated as $Co_4\mathbf{LV5t}Cl_4(H_2O)_5$, was collected as a very fine brown-green powder after the bright green filtrate had been set aside for one day. When another reaction

was carried out with added TEA a large amount of complex **24**, proposed to be Co_4**LV5t**$Cl_5(H_2O)_{1.5}$, was isolated as a pale brown solid.

Table 4·15 :
Selected ions (FAB-ms) for Co -LV5t - Cl complexes

		22	23	24
Co_4**LV5t**Cl_7O	1068			1064
Co_4**LV5t**Cl_6	1017			1026
Co_3**LV5t**$Cl_6(OH)_2$	993			990
Co_4**LV5t**Cl_5	982			
Co_3**LV5t**Cl_7	994			
Co_3**LV5t**Cl_5	926	926		
Co_4**LV5t**Cl_4	948			951
Co_4**LV5t**Cl_3	913			915
Co_4**LV5t**Cl_2O	894		898	890
Co_3**LV5t**Cl_3O	871	871	871	
Co_4**LV5t**O	859			859
Co_3**LV5t**Cl_2O	836	836	836	
Co_3**LV5t**Cl_2	820			820
Co_3**LV5t**ClO	799	799	799	
Co**LV5t**Cl_3	771	773	773	
Co_3**LV5t**O	765			765
Co**LV5t**Cl_3	738	737		
Co_2**LV5t**Cl	725			727
Co**LV5t**Cl_2	701	700	700	

These complexes do not appear to incorporate the μ_4-OH or μ_4-O (fragments incorporating these are not found in the FAB-ms) seen in many other tetranuclear complexes of this ligand system and this may explain their easier recovery and the greater yields compared to other products. With the above formulations complexes **22** and **24** would each contain three Co(II) and one Co(III) ions whereas all the metal ions in complex **23** would be Co(II).

6 : THE THIOCYANATE COMPLEXES

Table 4·16 : Thiocyanate complexes with LV5

25	Co_4**LV5**$Cl_4(NCS)_2(CH_3OH)_2$
26	Co_4**LV5**$Cl(NCS)_4(CH_3CH_2OH)(CH_3OH)H_2O$

Cobalt thiocyanate had been prepared by the method of Schlessinger [209]

and was used as the metal salt in a series of reactions. Although thiocyanate was the only anion added to these reaction mixtures it was still expected that chloride would be present for the reasons already discussed.

Table 4·17 :
Selected ions (FAB-ms) for Co - NCS - LV5 complexes

		25	26
Co_4**LV5**$(NCS)_5Cl_4H$	1155		1155
Co_4**LV5**$(NCS)_4Cl_4H$	1097		1099
Co_4**LV5**$(NCS)_5Cl_2 2H$	1086	1086	
Co_4**LV5**$(NCS)_4ClH$	992	992	
Co_4**LV5**$(NCS)_2OH$	857	856	
Co_4**LV5**$(NCS)Cl$	817	814	821
Co_4**LV5**$(NCS)O$	798	798	797
Co_4**LV5**$(NCS)H$	782	782	
Co_4**LV5**ClH	760		762
Co_2**LV5**$(NCS)Cl$	700		702
$Co_2(H_2$**LV5**$)(NCS)$	666		666
$Co_2(H_2$**LV5**$)Cl$	643		643

Both the above tetranuclear complexes came from preparations which varied from the standard synthesis; this yielded binuclear cobalt complexes which are discussed in the next chapter. When TEA was included in the reaction mixture a tetranuclear $Co_2^{II}Co_2^{III}$ complex analysing as Co_4**LV5**$Cl_4(NCS)_2(CH_3OH)_2$, (complex **25**) was isolated. This particular mixed valence system is another of those that it was hoped to synthesise in this project. The addition of TEA enhances deprotonation of the alcohol and phenol groups and in this case appears to have encouraged the formation of a tetranuclear product.
The only other tetranuclear complex, **26** Co_4**LV5**$Cl(NCS)_4(CH_3CH_2OH)_2$ $(CH_3OH)H_2O$ resulted from a very dilute reaction. It has already been noted that the only tetranuclear product from the perchlorate reactions also came from a high dilution reaction. It is considered that the thiocyanate product will have formed for the same reasons. This preparation was carried out because it was hoped that at high dilution a crystalline product might form. It did not.

7 : THE NITRATE COMPLEXES

7·1 : Nitrate complexes with LV5

Table 4·18 : Nitrate complex with LV5

27	$Co_4(\mu_4\text{-}OH)$**LV5**$Cl(NO_3)_5(CH_3OH)_2$

Complex **27** was recovered as a bright orange powder. On the basis of the chemical analysis the formula $Co_4(\mu\text{-}O)$**LV5**$Cl(NO_3)_5(CH_3OH)_2$ has been assigned to this product. A peak for the $[Co_4(\mu\text{-}O)$**LV5**$Cl(NO_3)_5]$ fragment is seen in the FAB-ms. This would mean that this also includes four Co(III) ions.

7·2 : Nitrate complexes with LV5t

Table 4·19 : Nitrate complexes with LV5t

28	$Co_4(\mu_4\text{-}O)$**LV5t**$Cl_3(NO_3)_2(CH_3CH_2OH)H_2O$
29	Co_4**LV5t**$(NO_3)_3(NCS)_3)(TEAH^+)(H_2O)_5$
30	Co_4**LV5t**$(NO_3)_3(NCS)_3Cl(TEAH^+)_2(H_2O)_2$

Table 4·20 :
Selected ions (FAB-ms) for LV5t - Nitrate complexes

		28	**29**
Co_4**LV5tO**$(NO_3)_4Cl_3$	1176	1174	
Co_4**LV5tO**$(NO_3)_2Cl_3$	1053	1053	
Co_4**LV5t** (NO_3)NCS·TEA	1029		1029
Co_4**LV5tO**$(NO_3)Cl_3$	990	990	
Co_4**LV5tO**(NO_3)		886	
Co_4**LV5tO**NCS	882		882
Co_4**LV5t**(NO_3)	870	869	
Co_4**LV5t**(NCS)	866		866
Co_4**LV5tO**Cl	842	839	841
Co_4**LV5tO**H	825	822	825

All the preparations using the *t*-butyl phenol produced tetranuclear compounds. The first reaction yielded the reddish-brown solid (complex **28**) formulated as $Co_4(\mu_4\text{-}OH)$**LV5t**$Cl_3(NO_3)_2(CH_3CH_2OH)H_2O$. When a second preparation was carried out in the presence of a slight excess (6 mmols) of TEA no products were isolated until NH_4NCS was added to the reaction mixture. TEA appears to

have been incorporated into the resulting tetranuclear complexes, designated as complex **29** Co_4**LV5t**$(NO_3)_3(NCS)_3(TEAH^+)(H_2O)_5$ and complex **30** Co_4**LV5t**$(NO_3)_3(NCS)_3Cl(TEAH^+)_2(H_2O)_2$, which were collected as a dark green powder and a microcrystalline black material respectively.

8 : CONCLUSION

Tetranuclear cobalt complexes have been formed with the **LV5** and **LV5t** ligand systems and this has been achieved with anions other than acetate. Mixed valence structures are common and access to the higher oxidation state complexes is available. These complexes appear to be oxidised by air and it is speculated that the oxidation process continues even in the solid products, as it has been noticed that many of these have darkened in colour in the time since they were first isolated.

One of the aims of the cobalt work was to fill in the gaps in the following series and this appears to have been been achieved. Complex **25** $[Co_4$**LV5**$Cl_4(NCS)_2]\cdot 2CH_3OH$ contains $Co(II)_2Co(III)_2$ and the $Co(III)_4$ has been achieved in both complex **10** $[Co_4(\mu_4\text{-}O)$**LV5**$Cl(CH_3COO)_3]\cdot CoCl_4^{2-}\cdot CH_3OH\cdot 4H_2O$ and complex **27** $Co_4(\mu\text{-}O)$**LV5**$Cl(NO_3)_5(CH_3OH)_2$. These complexes have not been structurally characterised by X-ray analysis and efforts to obtain suitable crystals will be part of future work.

Co_4^{II}	*	$Co^{II}Co_3^{III}$	*

Only two of the tetranuclear complexes have been assigned a formula containing four Co(III) ions and efforts are being made to obtain crystals to verify this assignment. It had been speculated that four Co(III) ions could not be accommodated by this ligand system. The geometry around the cobalt ions would be the most important limiting factor and certainly with bridging acetate ions once three Co(III) ions were incorporated the twist of the macrocycle meant that the geometry required for inclusion of a fourth Co(III) could not be achieved. However, with non-bridging anions four Co(III) ions could be accommodated in a planar system and it is now thought that this has been

achieved. When analysis results have implied that four Co(III) may be present these complexes have been checked using NMR but the results have not been definitive. It is noted that this technique would only be conclusive if no extraneous Co(II), either as an impurity or as $CoCl_4^{2-}$, were present.
One of the major difficulties of this work has been that the solids isolated from the reaction mixtures often appear to contain more than one product and it has been very difficult to separate these. It would seem that in many cases the different products have differing solubilities and this could be the key to their separation. It seems more likely that separation will be achieved by the use chromatographic techniques. Continuing work includes investigating separation procedures.

Future work will include the reduction of this ligand to see if with the more flexible tetraamine ligand four Co(III) ions could be more readily included.

EXPERIMENTAL

1 : THE COBALT ACETATE COMPLEXES

LV5 Complexes

Complex 8 : $[Co_4(\mu_4\text{-}O)LV5(CH_3COO)_4]\cdot Cl\cdot 3H_2O$

The $Co(CH_3COO)_2$ was dissolved in 20 mL dry MeOH to form a purple solution which was refluxed 10 mins after which time a solution of dfmp dissolved in 10 mL of MeOH and 30 mL of EtOH was added. The $dahpCl_2$ was dissolved in 10 mL of MeOH and after the KOH was added the mixture was sat in ice for 4 h. After addition of the dahp the reaction mixture was refluxed for 67 h. No solid was evident after this time. After two weeks of slow evaporation no solid had appeared so the reaction mixture was evaporated to dryness under vacuum and CH_3CN added. The undissolved material, 0·19 g of a khaki powder was collected in a filter paper and left to air dry. IR showed the formation of a macrocyclic complex but peaks at 1450, 1415 ⇒ there is a considerable amount of unreacted cobalt acetate present. Analysis* indicated that this was a mixture of products. The dark brown filtrate was placed. in a conical flask, into a jar of ether. Thirteen days later large black crystals were noticeable around the solvent line and amongst brown powder on the bottom of the flask. The crystals of **8** were separated by hand.

IR : 3410, 2907, 1642, 1558, 1448, 1386, 1326, 963, 925, 889, 821, 719 cm^{-1}

FAB-ms ($^m/_e$) : 976·1(100), 917·0(32), 857·9(68), 797·0(91), 737·9(49)

Parent (also base peak) = $[Co_4(\mu_4\text{-}O)\mathbf{LV5}(CH_3COO)_4]$

All other peaks represent sequential losses of acetate ions.

Analysis for : $[Co_4(\mu_4\text{-}O)\mathbf{LV5}(CH_3COO)_4]\cdot Cl\cdot 3H_2O$

Calculated :	C : 40·56;	H : 4·73;	N : 5·26 %
Found :	C : 40·68;	H : 4·78;	N : 5·25 %

Complex 9 : $[Co_4(\mu_4\text{-}O)LV5(CH_3COO)_4]\cdot Cl\cdot 3H_2O\cdot CH_3CH_2OH$

The powder **9** was collected separately from the **8** crystals.

Yield : 0·102 g, 0·186 mmol, 18·6 %

IR : 3408, 2922, 2864, 1638, 1557, 1448, 1421, 1076 cm^{-1}

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* Found : C : 27·24; H : 3·93; N : 3·50 %

FAB-ms ($^m/_e$) : 994·2(12), 976·1(100), 952·1(18), 917·1(45), 906·1(10), 858·0(98), 799·1(100), 738·0(49)

994·2 = $[Co_4(\mu_4\text{-}O)\mathbf{LV5}(CH_3COO)_4]\cdot Cl$

976·1 = $[Co_4(\mu_4\text{-}O)\mathbf{LV5}(CH_3COO)_4]$

Analysis for : $[Co_4(\mu_4\cdot O)\mathbf{LV5}(CH_3COO)_4]\cdot Cl\cdot 3H_2O\cdot CH_3CH_2OH$

Calculated :	C : 40·81;	H : 4·91;	N : 5·14;
Found :	C : 40·80;	H : 4·96;	N : 5·15;

Complex 10 : $[Co_4(\mu_4\text{-}O)LV5Cl(CH_3COO)_3]\cdot CoCl_4^{2-}\cdot CH_3OH\cdot 4H_2O$

A dahp solution was made by separately dissolving $daphCl_2$ (4 mmol, 0·746 g) and KOH (8 mmol, 0·224 g) in 15 mL of 3 : 2 MeOH : EtOH (dry). After precipitation of the KCl, the dahp solution was added to cobalt acetate tetrahydrate which had been stirring, but had not dissolved, in 40 mL of dry EtOH for 20 mins. The deep red solution was refluxed for 24 h, and left standing at ambient temperature for 6 days. As no solid had appeared the volume was reduced by three-quarters and an excess of LiCl added. After 3 days a very fine dark brown powder (0·45 g) was collected. This material appeared to be a mixture of products. Over time the filtrate lost most of its solvent to become a deep green sticky mass. Half of the dried filtrate was stirred in a $MeOH/H_2O$ mixture and very little dissolved. The undissolved solid was filtered off and aliquots of the filtrate were set up for ether diffusion. From one of these a deep olive green microcrystalline solid **1·1b** was eventually collected.

Yield : 0·07 g, 0·06 mmol, 6 %

IR : 3419, 2924, 1641, 1576, 1441, 1316, 1237, 960, 887, 820, 761 cm^{-1}

FAB-ms ($^m/_e$) : 952(100), 858(8), 796(13), 738(7).

952 = $[Co_4(\mu_4\text{-}O)\mathbf{LV5}Cl(CH_3COO)_3]^+$

UV (DMF) : 328sh, 405 (1·75)

Analysis for : $[Co_4(\mu_4\text{-}O)\mathbf{LV5}Cl(CH_3COO)_3]\cdot CoCl_4^{2-}\cdot CH_3OH\cdot 4H_2O$

Calculated :	C : 33·64;	H : 4·27;	N : 4·48 %
Found :	C : 33·42;	H : 4·25;	N : 4·45 %

Complex 11 : $[Co_4LV5Cl_4(CH_3COO)_3]$

The cobalt acetate and dfmp were mixed in ~ 40 mL dry EtOH. The dahp solution was made using a preprepared KOH solution and was sat in ice 5 h to precipitate the maximum amount of KCl. The dark brown reaction mixture was refluxed 63·25 h, (some solid was evident around the solvent line after 2 h of

refluxing), and filtered hot. The black crusty solid **1·1c** was collected and washed.

Yield : 0·41 g, 0·38 mmol, 38 %

IR : 3006, 2919, 2854, 2821, 1642, 1628, 1608, 1554, 1403, 1326, 1237, 965, 891(spl), 816, 772 cm^{-1}

FAB-ms ($^m/_e$) : 1074(22), 1016(56), 980(100), 906(56), 867(70), 775(67), 738(59).

Analysis for : $[Co_4$**LV5**$Cl_4(CH_3COO)_3]$

Calculated :	C : 39·14;	H : 3·96;	N : 5·37 %
Found :	C : 38·85;	H : 3·67;	N : 5·37 %

UV (DMF) : (just bumps) 688(0·2752), 616 (0·4318), 590(0·5151), 343(1·1799)

1·2 : THE COBALT ACETATE - THIOCYANATE COMPLEXES

LV5 Complexes

Complex 12 : $Co_4(\mu_4\text{-}O)$LV5$(NCS)_4(CH_3COO)(CH_3CH_2OH)_{1.5}(H_2O)_2$

The reaction was set up as for the previous one but with double the quantity of reactants. The reaction mixture was refluxed under N_2 for 24 h, left to cool to ambient temperature, and then reduced under N_2 to half the original volume. After 3 days the solution was further reduced, under N_2, to half. A pinkish brown powder (0·39 g) formed, was collected and washed with 2 x 10 mL dry EtOH. The IR showed this to be inorganic. After 3 weeks a further 0·04 g of inorganic product was collected from the deep green-brown filtrate. When after a period of time, no further solid was formed an excess of NH_4NCS and some dry EtOH was added to the remaining brown filtrate and the mixture stirred for 2 h. A bright green powder (complex **12**) formed and was washed and collected.

Yield : 1·66 g, 1·574 mmol, 78·69 %

IR : 2069, 1642, 1578, 1444, 1317, 1237, 961, 889, 823, 762 cm^{-1}

FAB-ms ($^m/_e$) : 975(100), 917(72), 858(44), 799(33), 738(18).

975 = (**LV5,** 4Co, O, 4NCS, H^+)

Analysis for : $Co_4(\mu_4\text{-}O)$**LV5**$(NCS)_4(CH_3COO)(CH_3CH_2OH)_{1.5}(H_2O)_2$

Calculated :	C : 39·15;	H : 4·36;	N : 9·77 %
Found :	C : 39·06;	H : 4·34;	N : 9·85 %

UV (DMF) : 380sh

Complex 13 : Co_4LV5$(NCS)_4(CH_3CH_2OH)$

NH_4NCS in MeOH was added to half of the dark brown filtrate of a cobalt acetate reaction and a green solid formed immediately. On refluxing this dissolved to form a deep green solution and after 24 h a small amount of khaki green powder (shown to be a mixture of products) was collected when the hot reaction mixture was filtered. The filtrate of was cooled at room temperature and the major product, a dark leaf green solid (complex **13**), was collected.

Yield : 0·38 g, 0·379 mmol, 38 %.

IR : 2067, ~1660(sh), 1642, 1576, 1550, 1443, 1352, 1315, 1234, 961, 867, 823, 761.

FAB-ms ($^m/_e$) : 975(100), 917(41), 858(24), 799(30).

Base peak (975) = **LV5** + 4Co + H_2O + 4NCS + H^+

UV (DMF) : 617, 585, 407.

Analysis for : Co_4**LV5**$(NCS)_4(CH_3CH_2OH)$

Calculated :	C : 40·73;	H : 3·82;	N : 11·18 %
Found :	C : 40·85;	H : 4·01;	N : 11·14 %

Complex 14 : $Co_4(\mu_4$-OH)LV5$(NCS)_4(NH_4NCS)(CH_3CH_2OH)$

A third product (complex **14**) a very dark green powder was collected from the filtrate of **13**.

Yield : 0·1 g, 0·093 mmol, 9 %.

IR : 2067, 1657, 1641, 1576, 1550, 1443, 1352, 1314, 1233, 959, 824, 760, 715 cm^{-1}

FAB-ms ($^m/_e$) : 1093(9), 1036(8), 975(100), 918(25), 859(21), 799(59).

Parent ion : $[Co_4(\mu_4$-O)**LV5**$(NCS)_4]H^+$

Analysis for : $Co_4(\mu_4$-OH)**LV5**$(NCS)_4(NH_4NCS)(CH_3CH_2OH)$

Calculated :	C : 38·97;	H : 3·92;	N : 12·98 %
Found :	C : 38·87;	H : 4·17;	N : 12·79 %

A tiny peak is found for this in the mass spectrum.

UV (DMF) : 621, 586, 413, 316sh.

LV5t Complexes

Complex 16 : $Co_4(\mu_4$-O)LV5t$(NCS)_4(CH_3COO)\cdot CH_3OH$

The $Co(CH_3COO)_2$ (4 mmol) and dftp (2 mmol) was dissolved dry MeOH and the golden-brown solution refluxed 30 mins. When the dahp solution was

added, the reaction mixture went brown. The reaction mixture was refluxed, without stirring, for 26 h. The reaction mixture was clear yellow with a brown crust around the solvent line. While cooling overnight the reaction mixture went brown. The reaction mixture yielded 0·008 g of pale brown powder which was completely used in a recrystallisation attempt. The IR of this material suggested it was tetranuclear. Half of the dark brown filtrate had excess NH_4NCS added and was stirred at room temperature for 2 h. The now dark green mixture was left to stand overnight and a green-brown powder (complex **16**) collected in a Hirsch funnel.

Yield : 0·05 g, 0·051 mmol, 5·1 %

IR : 3442, 2960, 2070(v sh), 1641, 1578, 1442, 1235, 957, 890, 837, 760, 715 cm^{-1}

FAB-ms ($^m/_e$) : 1059(100), 1001(47), 942(25), 881(28), 822(13)

Analysis for : $Co_4(\mu_4\text{-}O)$**LV5t**$(NCS)_4(CH_3COO)\cdot CH_3OH$

Calculated :	C : 42·86;	H : 4·54;	N : 9·76 %
Found :	C : 42·58;	H : 4·59;	N : 9·79 %

1·3 : THE COBALT ACETATE - AZIDE COMPLEXES

LV5 Complexes

Complex 15 : Co_4LV5$(N_3)_4Cl(CH_3COO)_2$

After filtering off the cobalt acetate complex from one of the cobalt acetate reaction mixtures, half the filtrate was refluxed and stirred with NaN_3 for 24 h. A reddish brown solid (complex **15**) separated, was collected by filtering and washed with 3 x 5 mL of dry MeOH.

Yield : 0·31 g, 0·297 mmol, 30 %.

IR : 3419, 2916, 2846, 2067(spl), 1641, 1562, 1453, 1404, 1384, 1318 cm^{-1}

FAB-ms ($^m/_e$) : 1074(69), 980(76), 906(93), 757(100), 698(69).

1073·94 : **LV5**, $3N_3$, 3Cl, CH_3COO^-, CH_3COOH

978·99 : **LV5**, $2N_3$, Cl, CH_3COO^-, H_2O

Analysis for : Co_4**LV5**$(N_3)_4Cl(CH_3COO)_2$

Calculated :	C : 36·75;	H : 3·66;	N : 21·43 %
Found :	C : 36·62;	H : 3·60;	N : 21·52 %

UV (DMF) :v. sl. bumps, 336sh

LV5t Complexes

Complex 17 : $Co_4(\mu_4\text{-}O)LV5t(N_3)_4(CH_3COO)_2$

The other half of the dark brown filtrate (from which complex **16** was collected) had excess NaN_3 added and was refluxed without stirring for 3 h and left to cool overnight. Two buff coloured powders (0·67 and 0·36 g) were sequentially collected by vacuum filtration. Analysis of the first product and the IR of the second showed them to be predominantly inorganic salts. The dark brown filtrate was set aside and dried to an olive green crust which barely dissolved when water was added to it. An olive green powder (complex **17**) was collected by vacuum filtration.

Yield : 0·02 g, 0·0203 mmol, 2 %

IR : 3422, 2958, 2870, 1637, 1560, 1480, 1325, 1235, 983, 954 cm^{-1}

FAB-ms ($^m/_e$) : 1113(61), 992(100), 928(71), 857(61), 787(86).

1113 = $[Co_4(\mu_4\text{-}O)\mathbf{LV5t}(N_3)_4]H^+$

Analysis : $Co_4(\mu_4\text{-}O)\mathbf{LV5t}(N_3)_4(CH_3COO)_2$

Calculated :	C : 45·89;	H : 5·27;	N : 9·86 %
Found :	C : 45·84;	H : 5·24;	N : 9·85 %

Complex 18 : $Co_4(\mu_4\text{-}O)LV5t(N_3)_{4.5}(Cl_{2.5})(H_2O)_2\cdot CH_3OH$

The two buff coloured solids (collected from the complex **17** reaction mixture) were stirred in a MeOH - EtOH - CH_3CN mixture to form a dark brown solution. Undissolved material (**18**) was filtered.

Yield : 0·169 g, 0·145 mmol, 15 %

IR : 2960, 2095, 1640, 1560, 1450, 1235, 975, 895, 840, 777 cm^{-1}

Analysis : $Co_4(\mu_4\text{-}O)\mathbf{LV5t}(N_3)_{4.5}(Cl_{2.5})(H_2O)_2\cdot CH_3OH$

Calculated :	C : 36·42;	H : 4·54;	N : 21·24 %
Found :	C : 36·37;	H : 4·24;	N : 21·05 %

2 : THE COBALT PERCHLORATE COMPLEXES

Complex 19 : $Co_4LV5Cl_3(ClO_4)(CH_3CH_2OH)_2\cdot H_2O$

This preparation was part of binuclear series in which only two metal equivalents were used. The $Co(ClO_4)_2$ (2 mmol) and the dfmp (2 mmol) were mixed in 40 mL of 1 : 1 dry MeOH : EtOH and the golden-brown solution refluxed 25 mins. The filtered dahp solution was prepared from $dahpCl_2$ (2

mmol) dissolved in 10 mL 1 : 1 dry MeOH : EtOH and KOH (4 mmol) solution. The dark brown reaction mixture was refluxed 24 h. The 0·09 g of dark yellow powder initially collected by vacuum filtration was shown, by IR, to be predominantly inorganic. The filtrate dried slowly to a brown crust, dry EtOH was added, a little dissolved to form a brown solution and the rest of the greenish brown solid (complex **19**) was collected in a frit.

Yield : 0·612 g, 0·578 mmol, 58 %.

IR : 1660, 1538, 1445, 1234, 1087, 869, 820, 769, 625

FAB-ms : 928(4), 871(11), 771(51), 714(7), 613(36), 568(11), 523(14), 468(100).

Analysis for : Co_4**LV5**$Cl_3(ClO_4)(CH_3CH_2OH)_2 \cdot H_2O$

Calculated :	C : 36·95;	H : 4·46;	N : 5·39 %
Found :	C : 36·97;	H : 4·45;	N : 5·13 %

3 : THE COBALT CHLORIDE COMPLEXES

LV5 Complexes

Complex 20 : $Co_4(\mu_4\text{-}O)$LV5$Cl_4(CH_3OH)(H_2O)$

$CoCl_2$ (4 mmol, 0·952 g) and dfmp (2 mmol, 0·382 g), dissolved in dry MeOH to form a pale green solution, were refluxed 25 mins. Dahp solution was added dropwise and the solution went brown with a brown solid forming around the solvent line within a very short time. The reaction mixture was refluxed 22 h after which time there was a fine solid evident in the green solution. The mixture was left to cool overnight and the volume reduced by half under vacuum. The products were a pale green powder (complex **20**) and a dark green crusty material (complex **21**) and these were separated by hand.

Yield : 0·129 g, 0·134 mmol, 13 %

IR : 3447, 2923, 1648, 1550, 1357, 1234, 895, ~850, 829, 773 cm^{-1}

FAB-ms ($^m/_e$) : 951(1), 924(2), 887(2), 852(3), 824(5), 789(6), 750(25), 715(10), 689(35), 653(100), 616(52), 554(9).

ES-ms ($^m/_e$) : 1396(11), 1384(6), 1281(7), 982(7), 887(9), 822(8), 759(12), 752(9), 690(54), 653(32), 635(12), 494(12), 327(67), 318(100)

Analysis for : $Co_4(\mu_4\text{-}O)$**LV5**$Cl_4)(CH_3OH)H_2O$

Calculated :	C : 37·69;	H : 4·14;	N : 6·06 %
Found :	C : 37·37;	H : 4·11;	N : 6·01 %

Complex 21 : Co_4LV5Cl_4·dahp·$4H_2O$·$2CH_3OH$

The dark green crusty material from the above reaction was collected and treated separately.

Yield : 0·198 g, 0·183 mmol, 18 %

IR : 1648, 1550, 1357, 1234, 895, ~850, 829, 773.

FAB-ms ($^m/_e$) : 995 (1), 951(1), 910(1), 887(1), 852(2), 815(4), 787(4), 750(31), 715(17), 689(23), 653(100), 616(50), 588(3), 554(9).
995 = [Co_4**LV5**Cl_4] + dahp + OH.

ES-ms ($^m/_e$) : 1097(16), 1063(26), 1048(12), 882(21), 826(15), 818(40), 759(22), 698(15), 693(25), 689(90), 653(69), 633(37), 591(22), 493(52), 464(23), 247(100)

Analysis for : Co_4**LV5**Cl_4·dahp·$4H_2O$·$2CH_3OH$

Calculated :	C : 38·19;	H : 4·53;	N : 7·07 %
Found :	C : 38·07;	H : 4·44;	N : 6·99 %

LV5t Complexes

Complex 22 : $Co_4LV5tCl_5(CH_3OH)(H_2O)_2$

The $CoCl_2$ (4 mmol) and dftp (4 mmol) dissolved in dry MeOH to form a pale green solution which was refluxed for 25 mins. A 2 mmol solution of dahp was added dropwise and the green solution refluxed for 22 h. After cooling the volume was reduced by half and a deep moss green powder **22** was collected by vacuum filtration.

Yield : 0·225 g, 0·214 mmol, 21 %

IR : 3414, 3156, 2955, 1653, 1548, 1356, 1236, 896, 859, 842, 773 cm^{-1}

FAB-ms ($^m/_e$) : 926(5), 871(40), 836(23), 799(13), 773(33), 737(100), 700(69), 638(13), 460(21).

Analysis for : Co_4**LV5t**$Cl_5(CH_3OH)(H_2O)_2$

Calculated :	C : 39·96;	H : 4·99;	N : 5·33 %
Found :	C : 40·02;	H : 4·98;	N : 5·36 %

Complex 23 : $Co_4LV5tCl_4(H_2O)_5$

The bright green filtrate of **22** was set aside and after 1 day a very fine brown-green powder was collected from this.

Yield : 0·506 g, 0·488 mmol, 49 %

IR : 3411, 2956, 1653, 1547, 1236, 896, 860, 843, 777 cm^{-1}

FAB-ms : 986(5), 898(15), 871(37), 836(45), 799(24), 773(32), 737(100), 700(77), 639(32), 573(11), 460(50).

Analysis for : Co_4**LV5t**$Cl_4(H_2O)_5$

Calculated :	C : 39·25;	H : 5·23;	N : 5·39 %
Found :	C : 39·21;	H : 5·23;	N : 5·55 %

Complex 24 : Co_4LV5t$Cl_5(H_2O)_{1.5}$

Dftp (2 mmol) and $CoCl_2$ (4 mmol) were dissolved in 100mL dry EtOH to form a blue solution. A 2 mmol dahp solution was added followed by 1 mL (a little over 6 mmol) of TEA added dropwise. The mixture was refluxed ~ 24 h and left to cool overnight. The deep brown reaction mixture contained some pale brown solid (complex **24**) which was pipetted onto filter paper and air dried.

Yield : 0·701 g, 0·694 mmol, 69 %

IR : 3283, 2942, 2904, 2837, 1638, 1559, 1320, 1228, 1115(triplet), 922, 884, 831, 771 cm^{-1}

FAB-ms ($^m/_e$) : 1064(28), 1026(40), 990(55), 951(28), 915(91), 890(54), 859(80), 820(100), 765(25), 727(36), 668(9), 580(18)

Analysis for : Co_4**LV5t**$Cl_5(H_2O)_{1.5}$

Calculated :	C : 40·32;	H : 4·68;	N : 5·53 %
Found :	C : 40·33;	H : 4·69;	N : 5·39 %

4 : THE COBALT THIOCYANATE COMPLEXES

Complex 25 : Co_4LV5$Cl_4(NCS)_2(CH_3OH)_2$

The $Co(NCS)_2$ was dissolved in 15 mL of dry MeOH and refluxed 10 mins. On addition of the dfmp solution (in 20 mL of dry MeOH) a green-blue solution formed. The dahpCl_2 was dissolved in 10 mL of MeOH, the KOH solution was added, and the mixture sat in ice for 4·5 h. The reaction mixture changed to brilliant deep green on addition of the dahp. As 1 mL of TEA (a little over 6 mmol) was added dropwise the reaction mixture became a green-brown colour. After refluxing 46 h the mixture was left to cool overnight. The product, a fine brown powder (complex **25**), was collected by dripping the reaction mixture through a frit. Some darker granular material, which dried and came free overnight, was left adhering to the flask walls. An IR was done separately on this material and all of this was used in recrystallisation attempts.

Yield : 0·635 g, 0·656 mmol, 66 %.

IR : 3432, 2921, 2855, 2069, 1638, 1558, 1353, 1321, 965, 882, 817, 768, 618 cm^{-1}

FAB-ms ($^m/_e$) : 1086(6), 992(6), 856(7), 814(15), 798(100), 782(10

1084 = **LV5** + 4Co + 5NCS + 2Cl

798 = **LV5** + 2Co + 3NCS + OH

Analysis for : Co_4**LV5**$Cl_4(NCS)_2(CH_3OH)_2$

Calculated :	C : 36·73;	H : 3·85;	N : 8·03 %
Found :	C : 36·59;	H : 4·00;	N : 7·90 %

Complex 26 : Co_4LV5Cl$(NCS)_4(CH_3CH_2OH)(CH_3OH)H_2O$

It was hoped that if the reaction was carried out in very dilute circumstances a crystalline product might result. The $Co(NCS)_2$ was dissolved in 100 mL of dry MeOH and refluxed 10 mins. The dfmp solution was made in 30 mL of dry MeOH and added. The dahpCl_2 was dissolved in 20 mL of MeOH, the KOH solution was added, and the mixture sat in ice for 3 h. The reaction mixture changed to a very deep green on addition of the dahp. After refluxing 48 h the mixture was left to cool slowly. No crystalline material formed but the product this time was a forest green powder (complex **26**). This was collected by vacuum filtration.

Yield : 0·148 g, 0·136 mmol, 14 %

IR : 3420, 2914, 2080, 1655, 1630sh, 1545 1355, 1235, 1120, 875, 826, 783, 626 cm^{-1}

FAB-ms ($^m/_e$) : 1155(6), 1099(6), 821(7), 797(9), 762(18), 725(8), 702(20), 666(32), 643(28), 607(100).

1155 = **LV5** + 4Co + 4Cl + 5NCS + H

607 = H**LV5** + 2Co

Analysis for : Co_4**LV5**$(NCS)_4Cl(CH_3CH_2OH)(CH_3OH)H_2O$

Calculated :	C : 39·18;	H : 4·44;	N : 9·88 %
Found :	C : 39·27;	H : 4·26;	N : 9·87 %

5 : COBALT WITH NITRATE

LV5 Complexes

Complex 27 : $Co_4(\mu\text{-OH})$LV5Cl$(NO_3)_5(CH_3OH)_2$

$Co(NO_3)_2$ (4 mmol, 1·164 g) and dfmp (2 mmol, 0·324 g) were mixed in ~ 100 mL of dry EtOH and the orange solution refluxed 25 mins. Dahp was added and the now yellow-brown reaction mixture refluxed for 20 h after which the

product, a fine bright orange powder (complex **27**), was collected by vacuum filtration.

Yield : 0·537 g, 0·467 mmol, 46·69 %

IR : 3422, 3143, 2921, 1653, 1632, 1543, 1384, 1359, 1307, 861, 817, 776 cm^{-1}

FAB-ms ($^m/_e$) : 1244(2), 1111(2), 1008(2), 952(22), 928(3), 852(2), 790(3), 711(2), 675(3), 641(4), 599(4·5), 550(5), 487(100). Belfast

FAB-ms ($^m/_e$) : 805·3(5), 775·1(10), 761·3(8), 745·1(7), 717·3(15), 673(20), 63(31), 607·0(72), 585·2(42), 541·2(59), 497·1(73), 460·0(93), 409·1(100)

1245 = **LV5** + 4Co + O + Cl +7NO_3
1112 = **LV5** + 4Co + O + 6NO_3

Analysis for : $Co_4(\mu\text{-OH})$**LV5**$Cl(NO_3)_5(CH_3OH)_2$

Calculated :	C : 31·32;	H : 3·59;	N : 10·95 %
Found :	C : 31·35;	H : 3·57;	N : 11·13 %

LV5t Complexes

Complex 28 : $Co_4(\mu_4\text{-O})$LV5t$Cl_3(NO_3)_2(CH_3CH_2OH)H_2O$

$Co(NO_3)_2$ (4 mmol, 1·164 g) and dftp (2 mmol) were mixed in ~ 100 mL of dry EtOH and a red solution formed immediately. Dahp was added the reaction mixture refluxed for 20 h after which a reddish-brown solid **28** was collected by vacuum filtration.

Yield : 0·55 g, 0·492 mmol, 49·15 %

IR : 3440, 2925, 1642, 1623, 1553, 1384, 970, 882, 834, 772 cm^{-1}

FAB-ms ($^m/_e$) : 1174(20), 1053(12), 990(58), 886(100), 86(88), 839(80), 822(98), 738(18), 578(12), 412(24).

1176 = **LV5t** + 4Co + O + 4NO_3 + 3Cl

1053 = **LV5t** + 4Co + O + 2NO_3 + 3Cl

Co analysis - 25·21%

Calc for : [Co_4**LV5t**$(\mu\text{-O})(NO_3)_2$] - 24·80%

Analysis for : $Co_4(\mu_4\text{-O})$**LV5t**$Cl_3(NO_3)_2(CH_3CH_2OH)H_2O$

Calculated :	C : 38·64;	H : 4·68;	N : 7·51 %
Found :	C : 38·79;	H : 4·73	N : 7·64 %

Complex 29 : Co_4LV5t$(NO_3)_3(NCS)_3(TEAH^+)(H_2O)_5$

$Co(NO_3)_2$ (4 mmol, 1·164 g) and dftp (2 mmol) were mixed in ~ 100 mL of dry MeOH and the golden solution refluxed 15 mins. Dahp was added and the now brown-black reaction mixture refluxed while 1 mL (a little over 6 mmol) of TEA was added dropwise. The mixture was refluxed for 26 h after which the product, a fine mud coloured powder (0·34 g) was collected by vacuum filtration. This was shown, by IR, to be predominantly inorganic. The dark brown filtrate had excess NH_4NCS added and was stirred at room temperature for an hour and left to sit overnight. A dark green powder (complex **29**) was collected.

Yield : 0·768 g, 0·572 mmol, 57 %

IR : 3432, 2960, 2070, 1638, 1560, 1384, 1234, 984, 890, 839, 762 cm^{-1}

FAB-ms ($^m/_e$) : 1029·0(14), 957·1(18), 895·2(47), 882·0(100), 866·0(30), 841·0(28), 825 (27).

Analysis for : Co_4**LV5t**$(NO_3)_3(NCS)_3(TEAH^+)(H_2O)_5$

Calculated :	C : 37·98;	H : 5·11;	N : 11·33 %
Found :	C : 37·83;	H : 5·12;	N : 11·54 %

Complex 30 : Co_4LV5t$(NO_3)_3(NCS)_3Cl(TEAH^+)_2(H_2O)_2$

After 4 weeks black microcrystalline material (complex **30**) had formed in the filtrate of **29** and was collected and washed with EtOH. The sample smelled strongly of TEA.

Yield : 0·017 g, 0·012 mmol, 1 %

IR : 3440, 2958, 2066, 1635, 1559, 1384 cm^{-1}

Analysis for : [Co_4**LV5t**$(NO_3)_3(NCS)_3Cl(TEAH^+)_2(H_2O)_2$

Calculated :	C : 40·74;	H : 5·58;	N : 11·63 %
Found :	C : 40·89;	H : 5·49;	N : 11·64 %

CRYSTALLOGRAPHY

Complex 8 : $[Co_4(\mu_4\text{-}O)LV5(CH_3COO)_4]\cdot Cl\cdot 3H_2O$

Empirical formula	$C_{36}H_{53}ClCo_4N_4O_{16.50}$	
Formula weight	1076·99	
Temperature	130(2) K	
Crystal colour	black-brown	
Crystal form	block	
Crystal size	0·70 x 0·48 x 0·2 mm^3	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9·588(2) Å	a = 90°
	b = 23·327(3) Å	b = 96.49°
	c = 19·878(2) Å	g = 90°
Volume, Z	4417·4(1) $Å^3$, 4	
Density (calculated)	1.619 Mg m^{-3}	
Absorption coefficient	1·610 mm^{-1}	
F(000)	2216	
Theta range for data collection	2·03 to 22.50°	
Limiting indices	$0 \le h \le 8$, $0 \le k \le 25$, $-21 \le l \le 21$	
Reflections collected	5654	
Independent reflections	5248 [R(int) = 0·0551]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5237 / 0 / 524	
Goodness-of-fit on F^2	1·052	
Final R indices [$I>2\sigma(I)$]	R1 = 0·0573, wR2 = 0·1389	
R indices (all data)	R1 = 0·0782, wR2 = 0·1654	
Largest diff. peak and hole	1·249 and -0·641 $e.A^{-3}$	

CHAPTER 5

THE BINUCLEAR COBALT COMPLEXES

1 : INTRODUCTION

In the course of this work, new 'diagonal' binuclear complexes (Fig. 5·1a) were discovered. **LV5** incorporates the longer pentanol chain and in the tetranuclear complexes (Fig. 5·1b) of this ligand the metals are bridged by both the phenolic and alcoholic oxygens. In contrast, these new binuclear complexes of **LV5** have the metals occupying only two of the potential coordination sites with these being diagonally opposite each other. The new diagonal binuclear complexes were characterised by single crystal X-ray structure analysis. While this work was in progress Robson reported[165] similar binuclear structures containing a diagonal acetate and a diagonal OH bridge. In the Robson complexes (Fig. 5·1c) only two of the four coordination sites are occupied and the two metals are bridged by the phenolic oxygens.

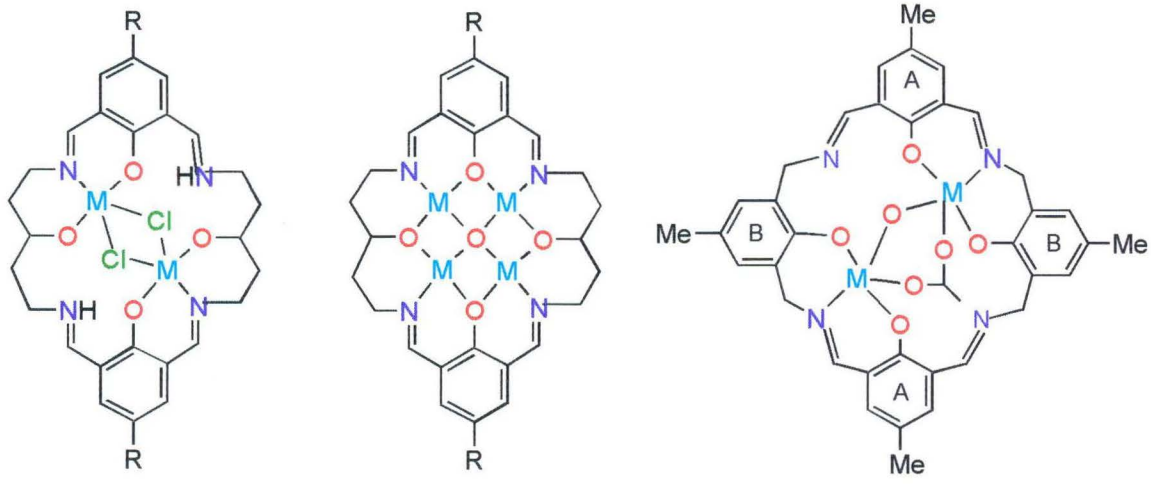


Fig 5·1 : a : The new diagonally bridged binuclear complex of LV5, b : Tetranuclear complex of LV5, c : The diagonally bridged Robson complex.

2 : THE PERCHLORATE COMPLEXES

2·1 : Perchlorate complexes with LV5

The **LV5** reaction mixtures, in which cobalt perchlorate was used as the templating metal salt, were usually golden-brown solutions. They were refluxed for 63 to 69 h over which time they became brown. Oblong golden crystals suitable for X-ray structure analysis were obtained from the filtered reaction mixtures of three different preparations. X-ray structure analysis of the first of these crystals (complex **31**) revealed the diagonally bridged binuclear complex $[Co_2(H_4\mathbf{LV5})Cl_2(H_2O)_2]\cdot 2ClO_4\cdot 2CH_3CH_2OH$ (Fig. 5·2).

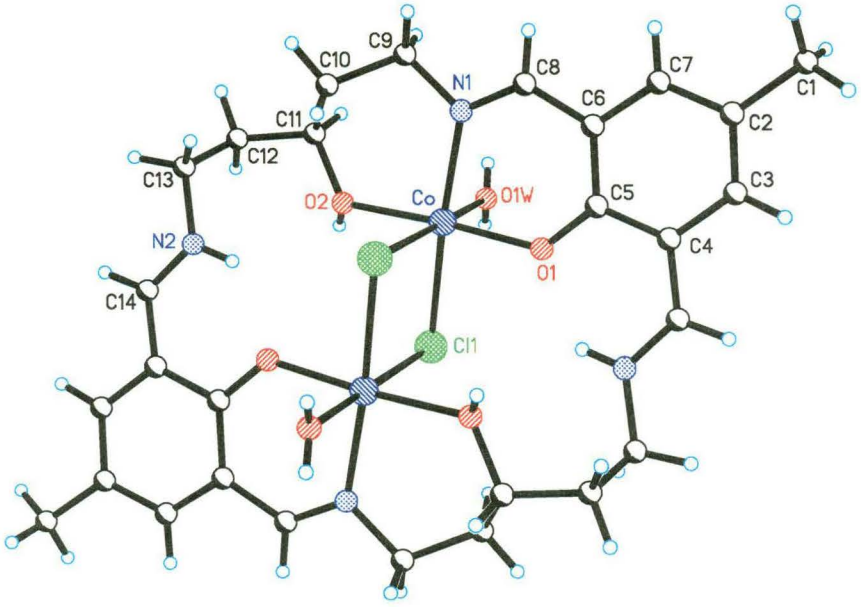


Figure 5·2 : The $[Co_2(H_4LV5)Cl_2(H_2O)_2]$·cation of complex 31.

The two cobalt ions are bound, by the phenol and alcohol oxygens and the imine nitrogen, diagonally from each other within the macrocyclic framework. The cobalt ion is 1·998(2) Å from the phenolic oxygen (O1), 2·095(2) Å from alcohol function (O2) and 2·164(2) Å from the water oxygen (O1W). The C····N bond length for the coordinated imine group (N1····C8) is 1·280(4) Å compared with 1·291(4) for the unbound imine; this presumably arises from loss of electron density towards Co^{2+}. Between the cobalts there are two bridging chloride ions. The Co····Cl distance is 2·501(1) Å which is considerably longer

than that found in complexes **M15** and **M16** where the Co····Cl distances are 2·28 and 2·27 Å respectively. The cobalt ions are designated Co(II) in all of these structures. This designation is supported by the charge balance of the complex, the bond lengths around the ions and the magnetic data. In contrast to the conventional binuclear complexes, all the oxygens are involved in binding to the metals, though none of them is bridging, the alcohol oxygens have remained protonated and a proton transfer from the phenol to the imine has occurred. There is hydrogen bonding between this proton and the phenolic oxygen (Fig 5·3).

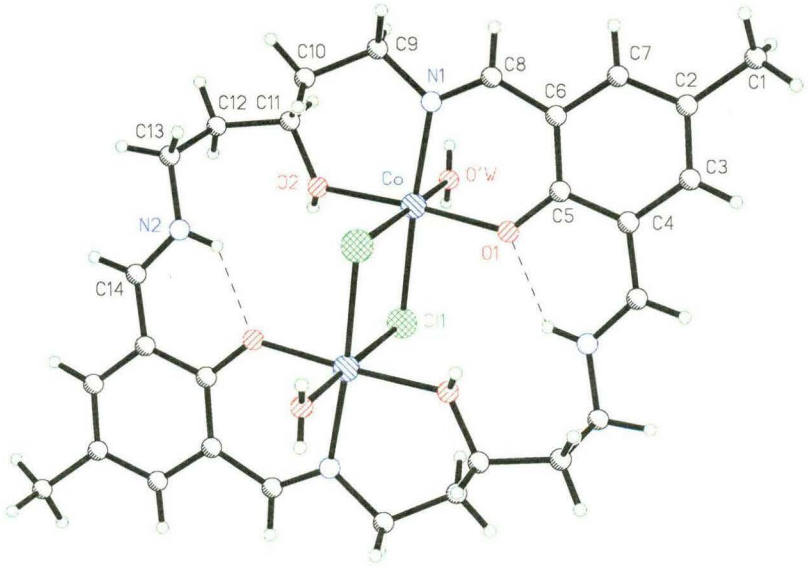


Figure 5·3 : The cation of complex 31 showing the internal H-bonding

The transfer of a proton from a dfmp head unit to an imine is not unprecedented. A similar transfer was seen in M^{c}Kee's mononuclear lead complex of **LV3**[42] and Nelson has reported that such a transfer occurs in her potentially dinucleating azacryptands[223,224] (formed from the Schiff base condensation of dfmp with tren) when they form mononuclear complexes. This transfer was intially discovered by NMR studies and later verified by X-ray crystal structure analysis. Under pH neutral conditions the cryptand was found to accommodate a metal ion in one potential site while the other site was occupied by three protons transferred from phenols to imino nitrogens. If the pH was adjusted then dinucleating complexes were formed. In the case of the cobalt macrocyclic complexes it is thought that the transfer occurs because

there is space available in the unoccupied site to accommodate the proton and pH is not considered to be an influencing factor.

The complex is distinctly "stepped"(Fig. 5·4). There is a centre of inversion in the molecule. Each phenolic portion of the macrocycle is planar (mean plane deviation is 0·017 Å) and parallel to the other one. The geometry around the cobalt ions is approximately octahedral with the coordination sphere being completed by a water molecule. Each chlorine is an axial donor to one cobalt and an equatorial donor to the other.

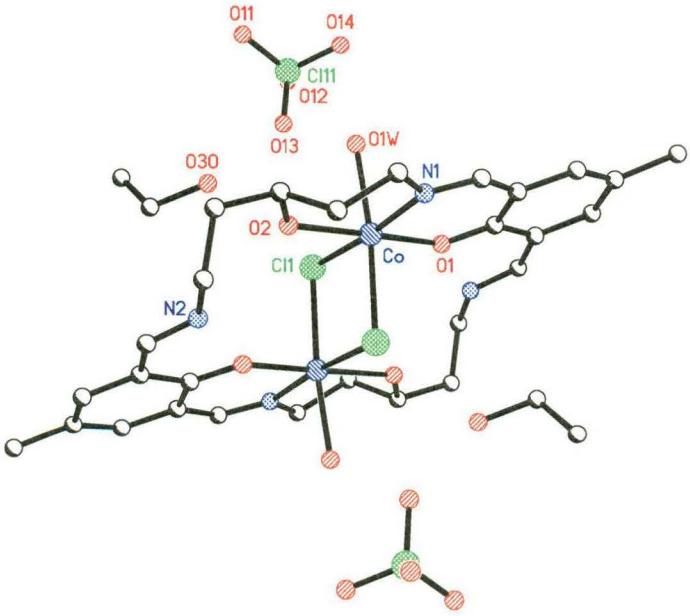


Figure 5·4

There was a small amount of disorder (~3 %) of the cobalt atoms in this structure and their alternate positions are shown in the following diagram (Fig. 5·5).

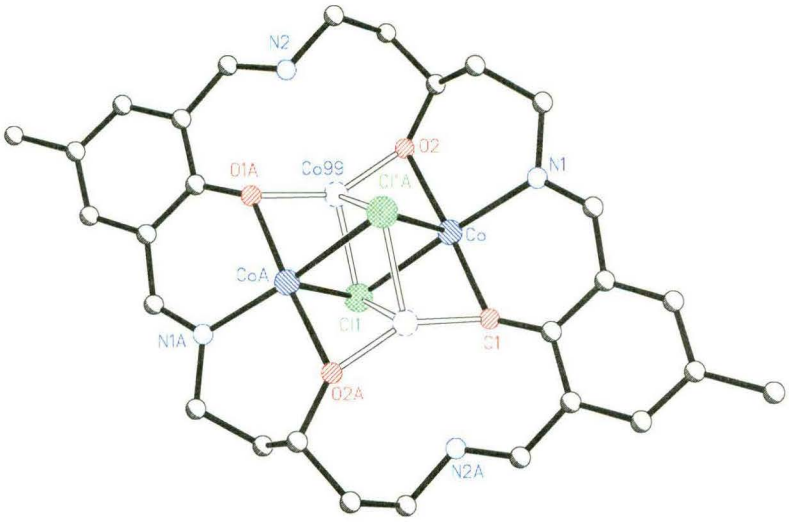


Figure 5·5 : Showing positions of the partial occupancy cobalt ions

A perchlorate anion and an ethanol molecule are found in the unit cell. The macrocycles are arranged in layers within the crystal structure and each perchlorate ion is hydrogen bonded (Fig. 5·6) to a water molecule on a macrocycle in two adjacent rows.

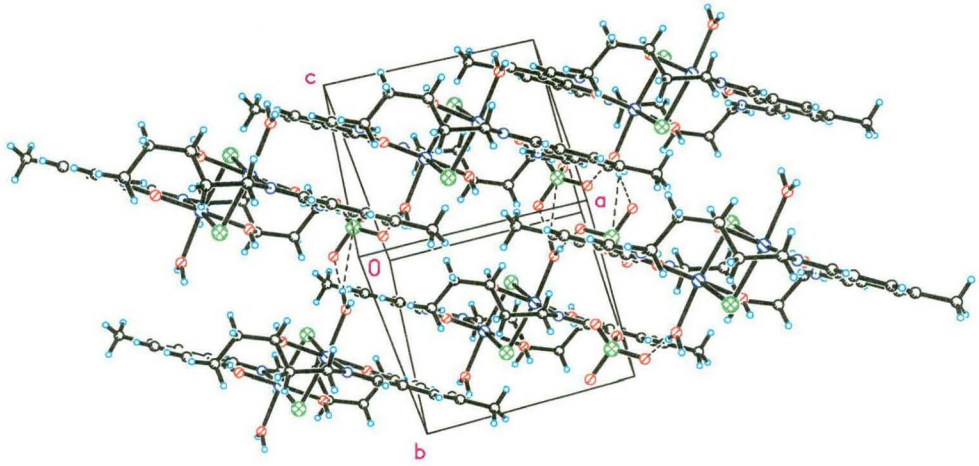


Figure 5·6

Details of the H-bonding are shown in Figure 5·7. O1WA is 2·830 Å from O13A and has the slightly longer interaction of 2·876 Å with O14B. Each alcoholic oxygen has an ethanol molecule coordinated at a distance of 2·684 Å

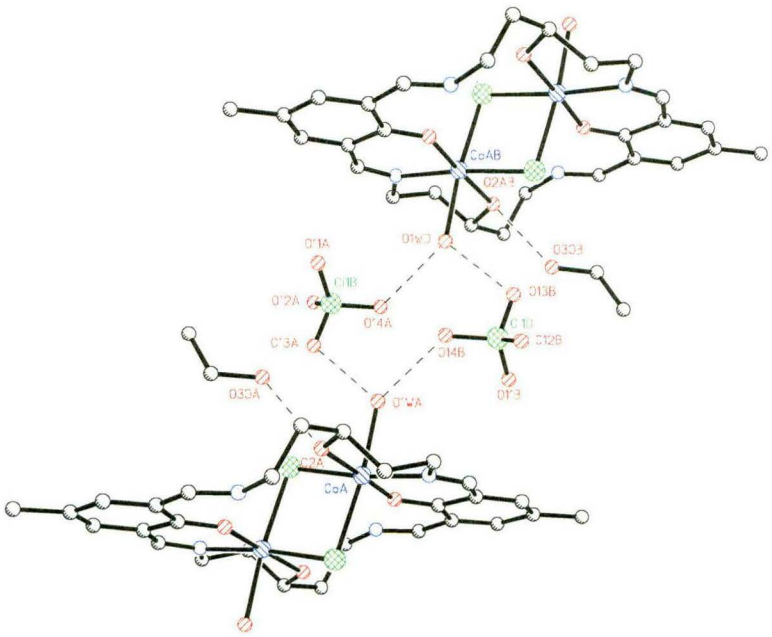


Figure 5·7 : H-bonding details for Complex 31

Table 5·1 : Selected bond lengths [Å] for 31 $[Co_2(H_4LV5)Cl_2(H_2O)_2]\cdot 2ClO_4\cdot 2CH_3CH_2OH$

Co-O1	1·998(2)	Co-O2	2·095(2)	Co-N1	2·112(2)
Co-O1W	2·164(2)	Co-Cl1	2·5007(10)	Co-Cl1#1	2·4831(12)
Cl1-Co99	2·197(4)	Cl1-Co#1	2·4831(12)	O1-Co99#1	1·900(10)
O2-Co99	1·734(9)	Co99-O1#1	1·900(10)		

Symmetry transformations used to generate equivalent atoms :

#1 -x+1,-y+2,-z+1

Table 2 : Selected bond angles [deg] for 31 $[Co_2(H_4LV5)Cl_2(H_2O)_2]\cdot 2ClO_4\cdot 2CH_3CH_2OH$

O1-Co-O2	175·79(9)	O1-Co-N1	90·45(9)
O2-Co-N1	93·69(9)	O1-Co-O1W	92·81(9)
O2-Co-O1W	86·71(9)	N1-Co-O1W	85·81(10)
O1-Co-Cl1#1	91·92(7)	O2-Co-Cl1#1	88·28(7)
N1-Co-Cl1#1	98·21(7)	O1W-Co-Cl1#1	173·77(7)
O1-Co-Cl1	88·05(6)	O1#1-Co99-Cl1	104·3(3)
O2-Co-Cl1	87·75(7)	N1-Co-Cl1	173·33(7)
O1W-Co-Cl1	87·77(8)	C5-O1-Co99#1	129·2(2)
C5-O1-Co	129·2(2)	C11-O2-Co99	149·9(3)
C11-O2-Co	123·8(2)	C8-N1-Co	123·5(2)
C9-N1-Co	121·7(2)	O2-Co99-Cl1	108·3(4)
O2-Co99-O1#1	146·1(3)		

Since a binuclear complex of this type had not been seen before, the reaction was repeated and this time a very small amount of inorganic salt was filtered from the golden-brown reaction solution. Oblong golden crystals formed in the filtrate within three days but had to be recrystallised three times before X-ray quality crystals were obtained. These crystals dissolved in CH_3CN to form a green solution. Initially square green crystals grew in this solution and were soon followed by oblong golden ones which looked very like the those of **31**. The green crystals decomposed before they could be investigated by X-ray analysis. A number of form and colour changes were noted throughout the investigation of the cobalt chloride and cobalt perchlorate complexes and the significance of these colours will be discussed later. A data set was collected for the oblong golden crystals (complex **32**) because initial X-ray investigations showed the cell not to be the same as **31**.

In complex **32** the macrocyclic portion is essentially the same as the first structure (Fig. 5·8) but with methanol molecules coordinated to the cobalts in place of water molecules. The two phenol rings show very little deviation from planarity (0·0058 Å for the C1 – C7 ring and 0·0053 Å for the C1a – C7a ring) and are almost completely parallel (dihedral angle of 0·1°) to each other.

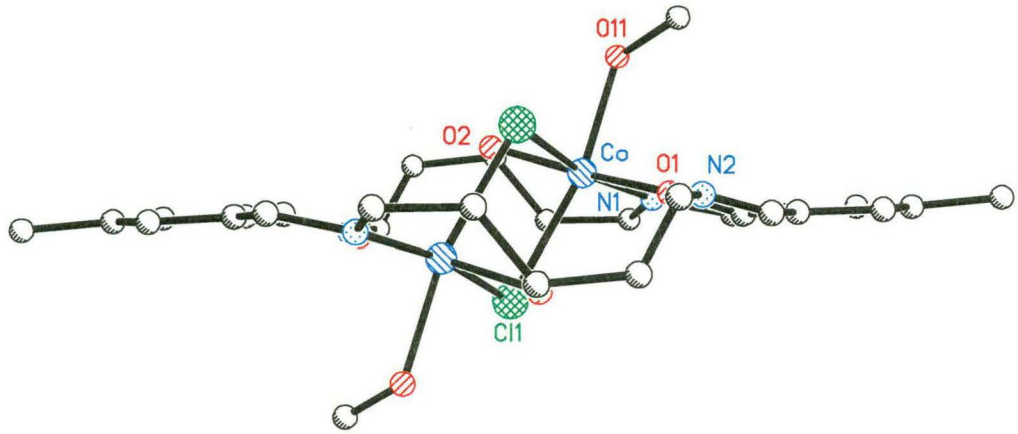


Figure 5·8 : The $[Co_2(H_4LV5)Cl_2(CH_3OH)_2]^{2+}$ cation of 32

The structure shown in Figure 5·8 proved to be quite a trap for a student crystallographer. At first appearances a tetranuclear complex (with other than acetate anions) had been formed but there were soon indications that this

could not be the case. Firstly, if the structure was tetranuclear it appeared to have a chloride ion tripodally associated with three of the cobalt ions and this did not make chemical sense. Secondly, if the model contained four cobalt and two chloride ions the temperature factors of two of the ions modelled as cobalts indicated that the electron density was too great for this to be correct. If modelled with two cobalts and four chlorides the temperature factors of two of the ions modelled as chlorides indicated that the electron density was too little. The solution (Figs. 5·9a and 5·9b) showed that this complex had crystallised in such a way that in 48% of the molecules the central cobalts and chlorides were in one orientation and in the other 52% they were arranged in the diagonally opposite manner. This is analogous to the 3% disorder shown in complex **31**.

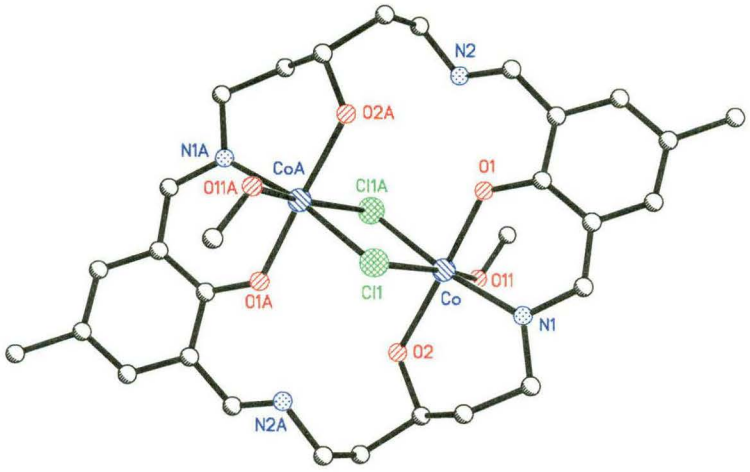


Figure 5·9a

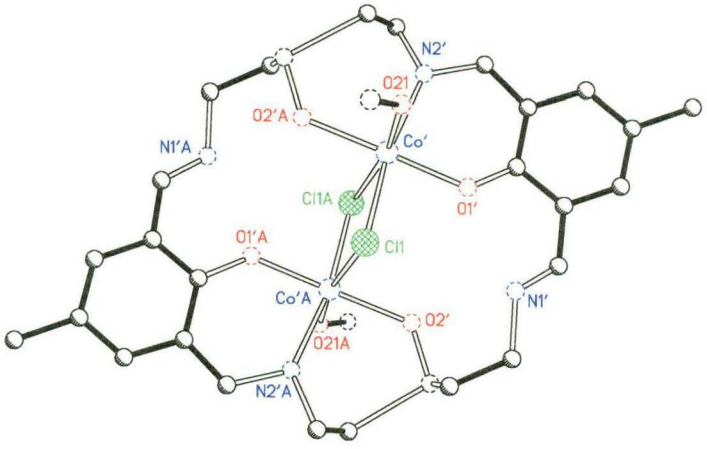


Figure 5·9b

Figure 5·10 shows these two superimposed on each other and it becomes quite clear how it was mistakenly thought (albeit fleetingly) to be a tetranuclear complex.

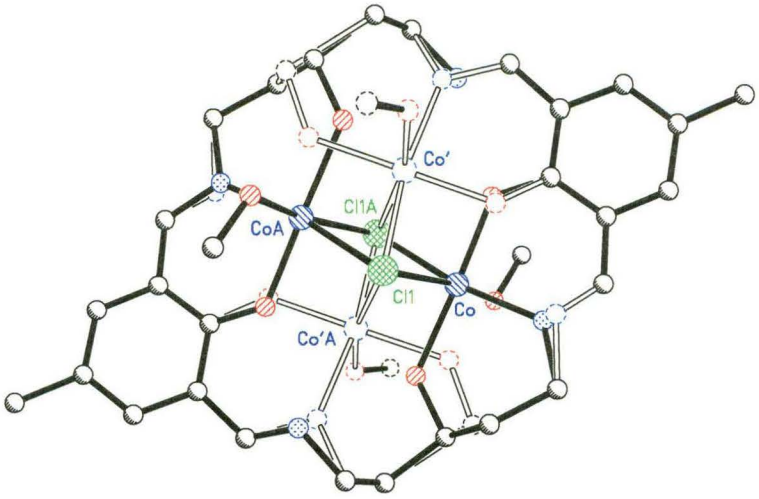


Figure 5·10

This figure also shows the disorder in the macrocyclic structure which is brought about by the alternate positions of the cobalt ions. There are alternate positions for the alcohol and phenol oxygens, the nitrogen atoms, and three of the carbons in each diamine chain.

Figures 5·11 and 5·12 show the H-bonding in the crystal packing of this compound. Once again the macrocycles are arranged in layers with the perchlorate molecule and the methanol molecule associated with each macrocycle found between these layers.

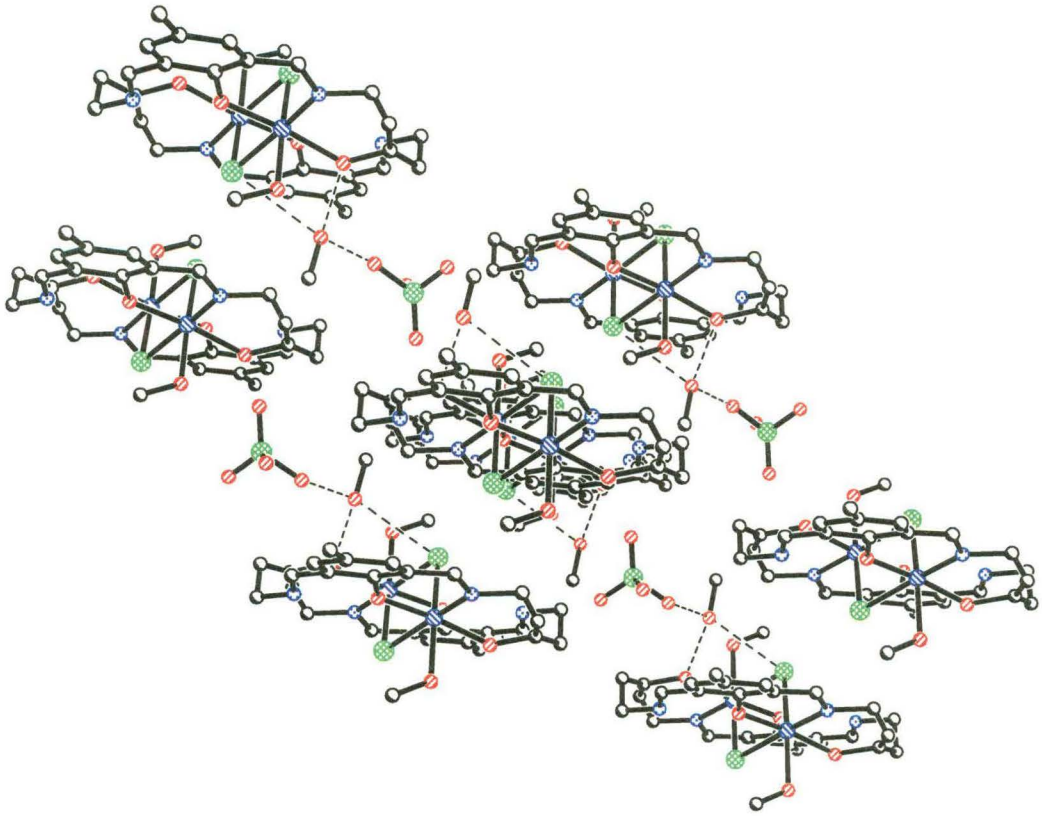


Figure 5·11

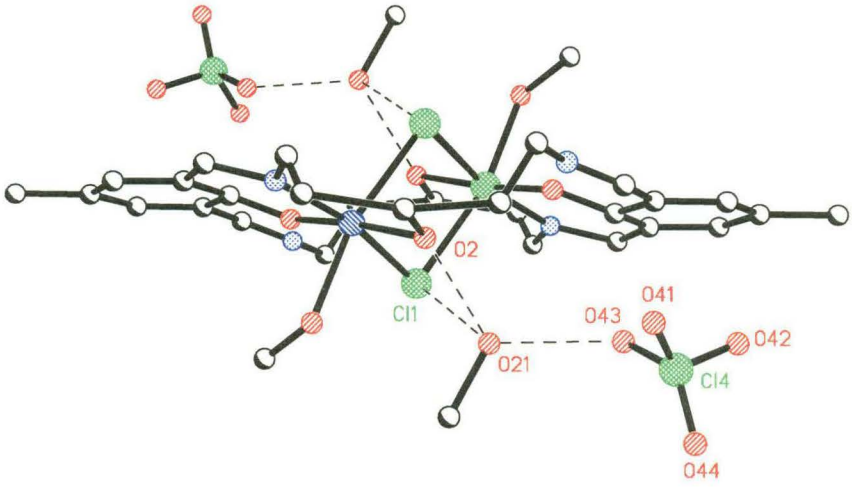


Figure 5·12 : Detail of the H- bonding interactions in complex 32

The methanolic oxygen bridges, by a hydrogen bonding interaction, an alcoholic oxygen in an adjacent macrocycle (O21 to O2 - 2·397 Å) and an oxygen in a perchlorate molecule (O21 to O43 - 2·661 Å). There is a weaker H-

bond of 3·200 Å from this oxygen (O21) to one of the chloride bridges (Cl1) in the macrocycle.

Table 5·3 : Selected bond lengths [Å] for $[Co_2(H_4LV5)Cl_2(CH_3OH)_2]\cdot 2ClO_4\cdot 2MeOH$

Co-O2'	1·61(2)	Co-O1	1·991(11)	Co-N1	2·06(2)
Co-O1'	2·141(13)	Co-O2	2·15(2)	Co-O11	2·139(12)
Co-Cl1#1	2·367(4)	Co-Cl1	2·548(4)	Co'-O2#1	1·62(2)
Co'-O1'	1·986(12)	Co'-O2'#1	2·06(2)	Co'-O1	2·133(11)
Co'-N2'	2·15(2)	Co'-O21	2·222(14)	Co'-Cl1	2·318(4)
Co'-Cl1#1	2·597(4)	Cl1-Co#1	2·367(4)	Cl1-Co'#1	2·597(4)
O2'-Co'#1	2·06(2)	O2-Co'#1	1·62(2)	O11-C21	1·46(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z+1

Table 5·4 : Selected bond angles [deg] for $[Co_2(H_4LV5)Cl_2(CH_3OH)_2]\cdot 2ClO_4\cdot 2MeOH$

O1-Co-N1	90·9(6)	C8-N1-Co	126·1(12)	O11-Co-Cl1	166·4(4)
C9-N1-Co	124(2)	C21-O11-Co	122·9(10)	C10-O2-Co	117·5(10)
O1-Co-O2	174·8(5)	N1-Co-O2	92·7(7)	O1-Co-O11	90·8(5)
N1-Co-O11	87·6(6)	O2-Co-O11	85·6(6)	O1-Co-Cl1	96·8(4)
O1-Co-Cl1#1	81·4(3)	N1-Co-Cl1#1	168·4(5)	C1-O1-Co	26·6(9)
O2-Co-Cl1#1	94·6(4)	O11-Co-Cl1#1	83·9(4)	O2#1-Co'-O1	144·4(6)
N1-Co-Cl1	103·5(5)	O2-Co-Cl1	86·1(4)		

A third repeat of this reaction yielded, in two days, oblong golden crystals from the filtered reaction solution and again an initial check revealed a different cell to both **31** and **32**. This complex **33** is very similar to complex **32** having a diagonally chloride bridged binuclear cobalt core with methanol molecules coordinated to the metal ions. The charge balance is satisfied by the presence of two unbound perchlorate anions. The complex differs in that no solvent molecules are found in the structure. Again the complex exhibits considerable disorder with the central cobalt and chloride ions being in one orientation in 41% of the molecules and and in the diagonally opposite orientation in the other 59 %. As a consequence of this, some disorder is also found in the rest of the complex. Figure 5·13 represents the partly refined structure (R1 = 11 %) where the disorder of the cobalt and chloride ions, the coordinated methanol molecules and two of the macrocyclic carbons is modelled.

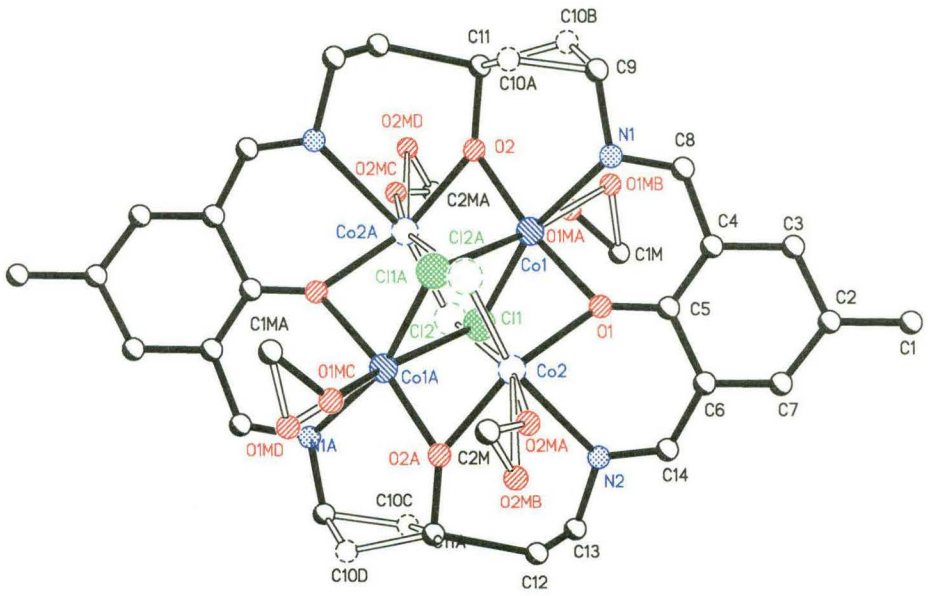


Figure 5·13 : The cation of Complex 33 : $[Co_2(H_4LV5)Cl_2(CH_3OH)_2]\cdot 2ClO_4$ showing some of the disorder

The packing diagram of complex **33** (Fig. 5·14) shows the macrocyclic cations arranged in rows with the perchlorate anions disposed between them. There is no evidence of hydrogen bonding in this strucuture.

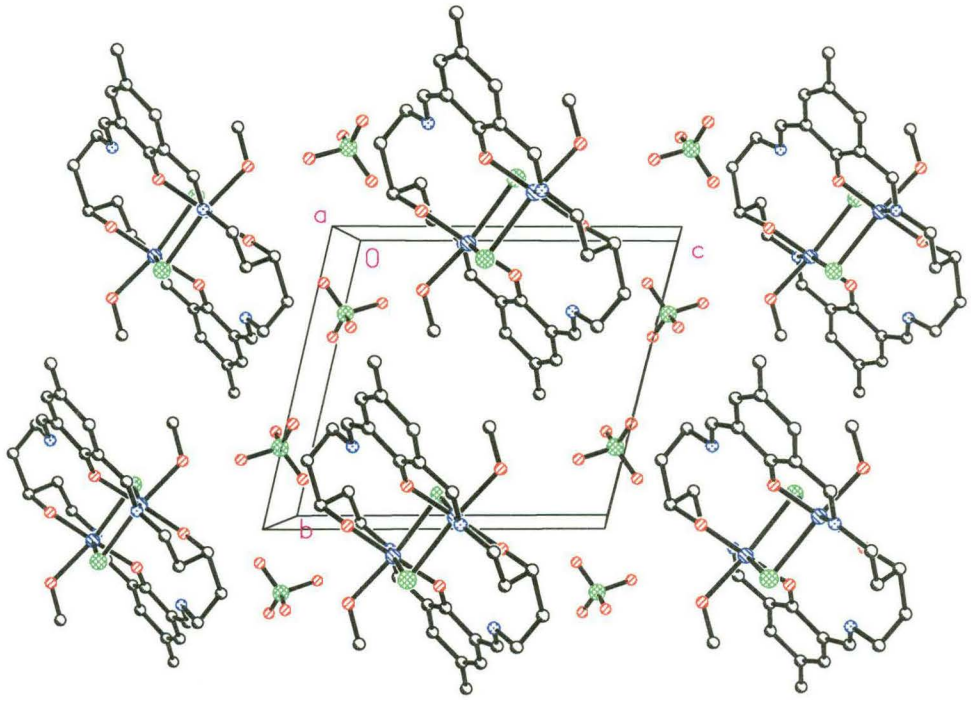


Figure 5·14 : Packing diagram of Complex 33

Table 5·5 : Selected bond lengths [Å] for $[Co_2(H_4LV5)Cl_2(CH_3OH)_2]\cdot 2ClO_4$

Co(1)-O(2)	1·902(9)	Co(1)-O(1)	1·986(7)	Co(1)-ClA	2·272(8)
Co(1)-N(1)	2·292(12)	Co(1)-ClB	2·515(8)	Co(1)-Co(2)	2·730(3)
Co(2)-O(1)	991(8)	Co(2)-ClA	2·485(9)	ClA-ClB	0·538(7)

Table 5·6 : Selected bond angles [deg] for $[Co_2(H_4LV5)Cl_2(CH_3OH)_2]\cdot 2ClO_4$

O(2)-Co(1)-O(1)	169·6(5)	O(2)-Co(1)-ClA	105·0(3)
O(1)-Co(1)-ClA	84·7(4)	O(2)-Co(1)-N(1)	90·4(3)
O(1)-Co(1)-N(1)	80·3(4)	ClA-Co(1)-N(1)	163·7(2)
O(2)-Co(1)-ClB	94·7(3)	O(1)-Co(1)-ClB	94·7(4)
ClA-Co(1)-ClB	11·5(2)	N(1)-Co(1)-ClB	175·0(3)
O(2)-Co(1)-Co(2)	135·9(2)	O(1)-Co(1)-Co(2)	46·7(2)
ClA-Co(1)-Co(2)	58·7(2)	N(1)-Co(1)-Co(2)	113·4(3)
ClB-Co(1)-Co(2)	63·0(2)	O(1)-Co(2)-ClA	79·1(5)
O(1)-Co(2)-Co(1)	46·6(2)	ClA-Co(2)-Co(1)	51·4(2)
ClB-ClA-Co(1)	111(2)	ClB-ClA-Co(2)	114(2)
Co(1)-ClA-Co(2)	69·9(2)	ClA-ClB-Co(1)	58(2)
Co(1)-O(1)-Co(2)	86·7(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1

Other products were also collected from these reaction mixtures and they are shown in Table 5·7.

Table 5·7 : Perchlorate complexes

31	$[Co_2(H_4\mathbf{LV5})Cl_2(H_2O)_2]\cdot 2ClO_4\cdot 2CH_3CH_2OH$
32	$[Co_2(H_4\mathbf{LV5})Cl_2(CH_3OH)_2]\cdot 2ClO_4\cdot 2CH_3OH$
33	$[Co_2(H_4\mathbf{LV5})Cl_2(ClO_4)_2]\cdot H_2O\cdot CH_3CH_2OH$
34	$[Co_2(H_4\mathbf{LV5})Cl_2(ClO_4)_2]\cdot H_2O + 8CoCl_2$
35	$[Co_2(H_4\mathbf{LV5})Cl_2(ClO_4)_2]$
36	$[Co_2(H_4\mathbf{Lo\text{-}s})Cl_2(ClO_4)_2]$
37	$[Co_2(H_4\mathbf{LV5})Cl_2(H_2O)_2]\cdot 2ClO_4\cdot 2CH_3CH_2OH\ 2H_2O$
38	$[Co_2(H\mathbf{Lo\text{-}s})(ClO_4)_{1\cdot 5}\ Cl_{0\cdot 5}]\cdot 4H_2O\cdot CH_3CH_2OH$
39	$[Co_2(H\mathbf{Lo\text{-}s})(ClO_4)Cl]\cdot 4H_2O\cdot 0\cdot 5CH_3CH_2OH$

In the reaction from which the crystals of complex **31** were recovered, the dark brown solution had initially yielded a pale yellow-brown powder the analysis of which indicates it to be complex **34** $[Co_2(H_4\mathbf{LV5})Cl_2]\cdot 2ClO_4\cdot H_2O + 8CoCl_2$, a mixture of a binuclear complex and inorganic salt. The filtrate from the complex **34** mixture was set aside for slow evaporation and dried to a deep orange glassy material only some of which redissolved in dry EtOH to form a moss green solution. The undissolved residue, collected by vacuum filtration, was in the form of dark-brown glassy chunks. The IR of these chunks had features found in the spectra of both tetranuclear and binuclear complexes. The FAB-ms of this product showed it to contain almost equal amounts of binuclear complexes based on the full and an open-sided ligand. Calculations for the chemical analysis for surmised binuclear, trinuclear or tetranuclear complexes of **LV5** were always high in N_2. When a calculation was done for a 50 : 50 mix of binuclear macrocyclic and open-sided complexes (based on the formulae attributed to complexes **35** $[Co_2(H_4\mathbf{LV5})Cl_2(ClO_4)_2]$ and **36** $[Co_2(H_2\mathbf{Lo\text{-}s})Cl_2(ClO_4)_2]$) the result was very close to that found. It is proposed then that this material is then a 50 : 50 mix of these complexes. The crystals of complex **31** (the first structure described in this section) came from the dark brown filtrate of this material.

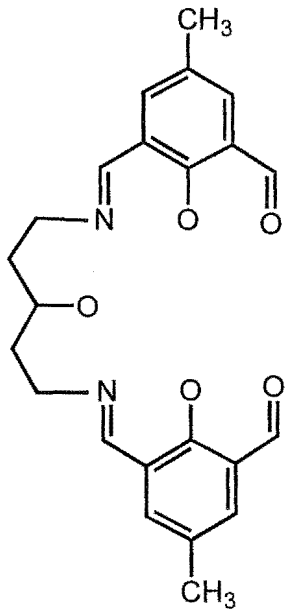


Figure 5·15 : The open-sided ligand

Figure 5·15 shows the proposed structure of the previously mentioned open-sided ligand. This structure was first postulated when a peak for this fragment was identified in many of the mass spectra of cobalt products. Its identification is a good example of the importance of good mass spectra in trying to characterise these compounds. Once it had been identified, many chemical analyses which had not been able to be matched to possible complexes of the full macrocycle, were shown to closely match complexes of this ligand. This ligand has potential for making unsymmetric systems in which the open side is closed with a diamine other than dahp. The IRs of complexes identified as incorporating this ligand show bands for C=O at ~ 1665. Mass spectra have also been invaluable in identifying those products which are a mixture of complexes. Most of these are shown to be mixtures of **Lo-s** with either some other binuclear or tetranuclear compound.

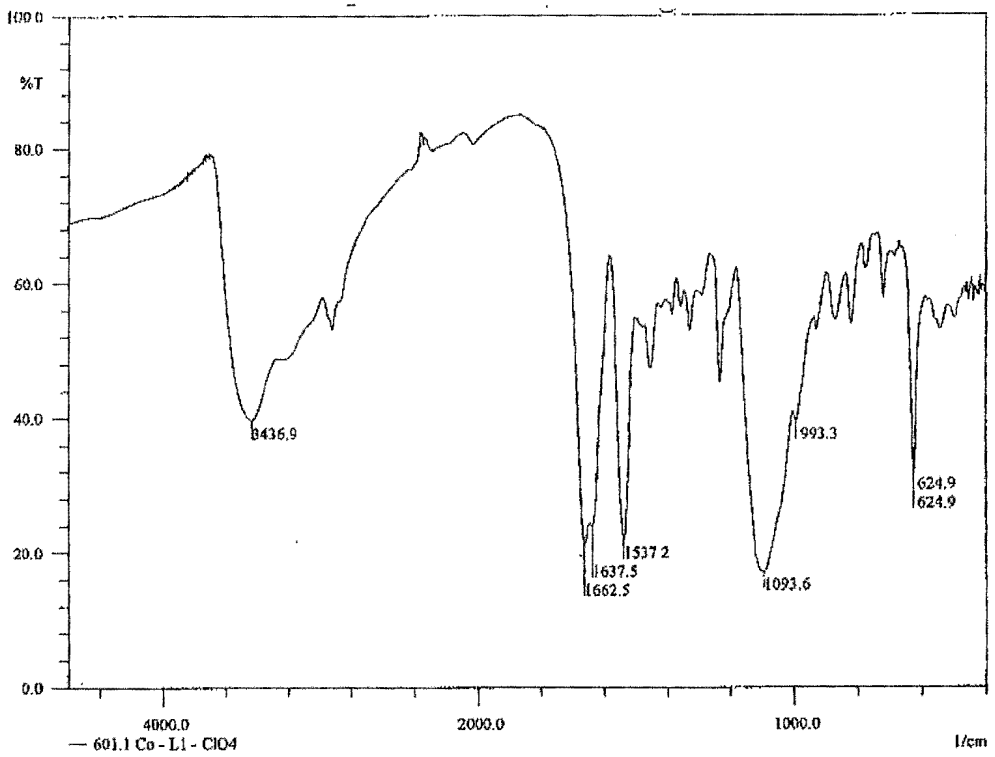


Figure 5·16 : IR of open-sided complex

The dried filtrate of complex **33** was stirred in MeOH and only some dissolved. The yellow powder residue (which has not been identified) was collected and the remaining solution set up for ether diffusion. After eleven days crystals

were collected from this filtrate. A unit cell check showed these to be the same as **33** and they were used for IR, FAB-ms and analysis.

Table 5·7 : Selected FAB-ms of LV5 - Cobalt - Perchlorate Complexes

		31	32	33	34	35-36	37	38	39
LV5, 4Co, O, $2ClO_4$, OH	954·87					952·1			
LV5, 4Co, 6Cl	933·76		931		934				
LV5, 4Co, $2ClO_4$	921·87	921·8							920·8
LV5, 4Co, 2Cl, ClO_4	892·96								891·8
LV5, 2Co, 2Cl, $2ClO_4$, H_2O	891·95								
H_2**LV5**, 2Co, 2Cl, $2ClO_4$	875·95	875				875·9			
H_4**LV5**, 3Co, 3Cl, ClO_4	872·92								
LV5, 4Co, 4Cl, 2H	865·66			866					
LV5, 4Co, ClO_4, Cl, H	858·90				859				
LV5, 4Co, 3Cl, OH	845·88								845·8
H_4**LV5**, 2Co, Cl, $2ClO_4$	842·97		843						
LV5, 4Co, 3Cl	828·88	830		828					827·8
H_3**LV5**, 2Co, 2Cl, ClO_4, H_2O, H	796·02	799·4				798			790·8
H_4**LV5**, 2Co, 2Cl, ClO_4	779·03		781			777·1			777·8
H_3**LV5**, 2Co, Cl, ClO_4, H_2O, H	762·07								763·8
H_4**LV5**, 2Co, 4Cl, H	751·02	753·4					752		
H_3**LV5**, 2Co, Cl, ClO_4	743·01		743			743·1			
H_2**LV5**, 2Co, ClO_4	707·07		709		707	707·1			
H_2**LV5**, 2Co, 2Cl	679·90		679		679		678		
H_3**LV5**, Co, ClO_4, H	650·15	650·5					650		652·8
H_3**LV5**, ClO_4, Cl, H_2O	643·19				643	643·1			
H_2**LV5**, ClO_4, Cl	624·17					623·9			
Lo-s, 2Co, ClO_4	623·97								
LV5, 2Co, H	607·11		607		607				
H_4**Lo-s**, 2Co, 2Cl	598·98							600	599·8
H_4**LV5**, ClO_4, 2H	593·23	593·6					593		
H_3**LV5**, Co, Cl, H	586·18	586·5							
H_2**Lo-s**, Co, ClO_4	567·05			568		568·1			561
H_3**LV5**, Co	550·19		550		550		550		
H_4**Lo-s**, Co, 2Cl	540·06					540·2			
Lo-s, 2Co	525·03			525		525·1			524·8
H_4**LV5**, H	493·28	493·6					493		
Lo-s, Co, OH	483·09					483·1			
H_2**Lo-s**, Co	468·11			468		467·1			
H_3**Lo-s**, Cl	445·15								445

FAB-ms suggests the powder residue to be a mixture of a tetranuclear product with no μ_4-O and four bound chloride ions and an open-sided complex. The fact that this was not soluble in MeOH is not surprising. It has been noticed, in the course of our study of this macrocyclic system, that the complexes which incorporate the μ_4-O or μ_4-OH group are much more likely to dissolve in MeOH or EtOH than those which don't. It is thought that solubility in these solvents

increases as the charge on the macrocyclic cation changes towards neutrality. This is supported by the fact that the compounds that dissolve in MeOH /EtOH are usually also soluble in CH_2Cl_2. Treatment of this powder with other solvents may be a route to separating its two components and is a possibility to be investigated in the future.

Another variation of the binuclear complex resulted when the synthesis was carried out in dry ethanol. The golden-brown mixture was refluxed for 120 h after which time the reaction mixture was still clear with the only visible solid being a little yellow powder coating the magnetic stirrer. The reaction mixture was filtered hot and within a few days masses of golden crystals of complex **37** analysing as $[Co_2(H_4\mathbf{LV5})Cl_2(H_2O)_2]\cdot 2ClO_4\cdot 2C_2H_5OH\cdot 2H_2O$ were visible in this filtrate. No crystal structure analysis was carried out on these crystals.

The source of the chloride ion in these structures would have to be the 1,5-diaminopentan-3-ol dihydrochloride. It appears that the efforts that have been made to exclude KCl from the reaction mixtures have not succeeded. To test this a "chlorine-free" reaction was tried. A slight excess (2·35 mmol) of dahp and 2 mmol of KOH dissolved instantly in water and the solution was quickly transferred to a separating funnel and extracted with three 5 mL aliquots of $CHCl_3$. The dahp containing $CHCl_3$ solution was added to a refluxing dfmp - $Co(ClO_4)_2$ mixture. Chunky golden crystalline-looking material and pinky-yellow needles formed after slow evaporation of this reaction solution. These were not only not the usual macrocyclic complex but did not appear to be just combinations of starting materials and metal salts. The IR indicated that some free carbonyl existed in these product. It would seem that a better approach to carrying out a synthesis in which chloride is totally excluded would be to try it using another salt of the diamine.

An attempt was made to make the nitrate salt of the diamine. The strategy was to synthesise the dahp as another salt by substituting a different acid for the concentrated HCl to cleave the phthalimide at that step of the synthesis (see p 93). Nitric acid was used but this was unsuccessful and a

number of unidentified products formed. It is known that primary aliphatic amines react with nitrous acid to yield diazonium salts[225] in the manner shown in equation 1. Aliphatic diazonium salts are quite unstable and break down to yield a complicated mixture of organic products. Nitrous acid, HONO, was possibly generated in the reaction medium to a small extent. Certainly the brown gas NO_2 was observed above the solution and in the reflux condenser. However, it does appear that it is possible to exchange another anion, e.g. BF_4, for the chloride but this is yet to be tried. It might also be possible to precipitate the chloride by using a silver salt.

$$\underset{\textbf{1° aliphatic amine}}{RNH_2} + {}^{*}NaNO_2 + HX \rightarrow [RN_2^{+}X^{-}] + H_2O \rightarrow N_2 + \underset{\textbf{alcohols + alkenes}}{\textbf{mixture of}}$$

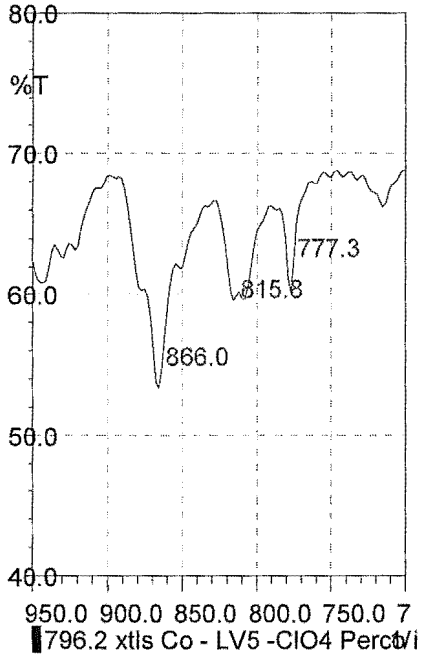
*$NaNO_2$ generates HONO

Equation 5·1

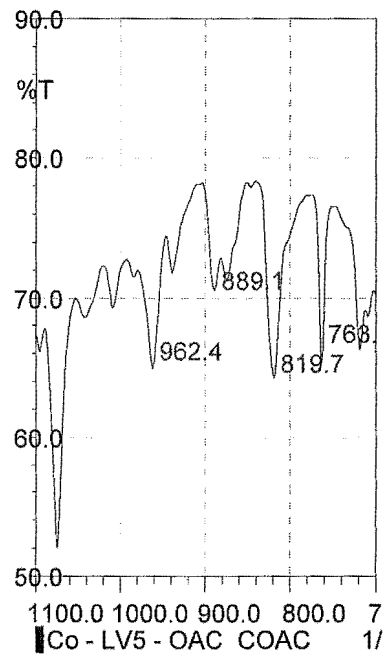
Since chloride ions were getting into the reaction anyway, it was decided to try using the 1,5-diaminopentan-3-ol-dihydrochloride directly without neutralisation or attempting to remove the chloride ions. The dahpCl_2, dissolved in MeOH, was added dropwise to the refluxing reaction mixture. The resulting solution was brilliant green rather than the usual golden colour. After 48 h of refluxing the entire reaction solution was set up for ether diffusion. The product was a brilliant emerald green oil in a bright ($CoCl_4^{2-}$?) blue solution. This oil has not been characterised and it could be that a different reaction has occurred on this occasion or that it just did not crystallise..

It often very difficult to tell from chemical analysis data if a tetranuclear or a binuclear complex had been formed. For example, the next time the cobalt perchlorate-**LV5** synthesis was tried it did appear that a tetranuclear complex had been made. Analysis results gave good agreement for [Co_4**LV5**$Cl(ClO_4)_4$] ·2$CoCl_4^{2-}$·6H_2O which chemically is impossible (unless a $Co(IV)Co(III)_3$ complex had been made!). The $CoCl_4^{2-}$ anion had been seen in the crystal structure of a

complex (**42**)* formed when cobalt chloride was the templating salt. However, a tetranuclear structure was not supported by the FAB-ms results where only binuclear ions were seen. The absence of a [Co_4O] fragment did not support a formulation containing this core. This led to a close examination of the IRs of all known tetranuclear and binuclear complexes made with both cobalt chloride and cobalt perchlorate. From these a fingerprint pattern could be discerned which appeared to distinguish these complexes. As well as the peaks already reported it was noticed that in the binuclear complexes a peak at ~1358 was generally seen and a triplet of peaks with a distinctive pattern (Fig 5·17a) were found at ~868, ~818 and ~718.



5·17a : Binuclear signature



5·17b : Tetranuclear signature

In contrast, in the tetranuclear products, a significant peak was found at ~1235 and a quartet (in the same region of the spectrum) with a different pattern was seen (Fig. 5·17b). From this it was obvious that this product was not tetranuclear but was also a binuclear product. This assignment was verified by all peaks in the FAB-ms being for the binuclear complex with various combinations of chloride and perchlorate ions. The product is proposed to be a mixture of a binuclear complex and a cobalt salt and needs further clean up.

---

* Complex 2·3a is discussed in detail in Section 3·1 of this chapter.

The use of these fingerprint patterns then became central to identification of the reaction products.

The products isolated from the **LV5** and cobalt perchlorate synthesis carried out in the presence of TEA have been formulated as **38** $[Co_2(H\mathbf{Lo\text{-}s})(ClO_4)_{1\cdot5}Cl_{0\cdot5}]\cdot4H_2O\cdot CH_3CH_2OH$ and **39** $[Co_2(H\mathbf{Lo\text{-}s})(ClO4)Cl]\cdot4H_2O\cdot0\cdot5CH_3CH_2OH$ being binuclear complexes of the open-sided ligand. These products were isolated when water was added to the reaction mixture.

3 : THE CHLORIDE COMPLEXES

3·1 : Chloride complexes with LV5

As chloride ions were present in the binuclear complexes formed when the metal salt was cobalt perchlorate it was decided to do a series of syntheses in which chloride was the only anion present. The reactions with cobalt chloride also yielded binuclear diagonally chloride-bridged structures, analogous to the perchlorate ones, and two of these have been characterised by X-ray structure analysis. The first of the crystals investigated were golden and similar in appearance to the binuclear cobalt perchlorate ones. These crystals formed in the dark brown solution filtered from the reaction mixture after refluxing for 64 hours.

X-ray crystal structure analysis of these revealed them to be of complex **40** $[Co_2(H_4\mathbf{LV5})Cl_2(CH_3OH)_2]\cdot2Cl\cdot2CH_3OH$ the cation of which is shown in Figure 5·18. The cationic structure is similar to complexes **32** and **33** with methanol groups coordinated to the cobalt ions.

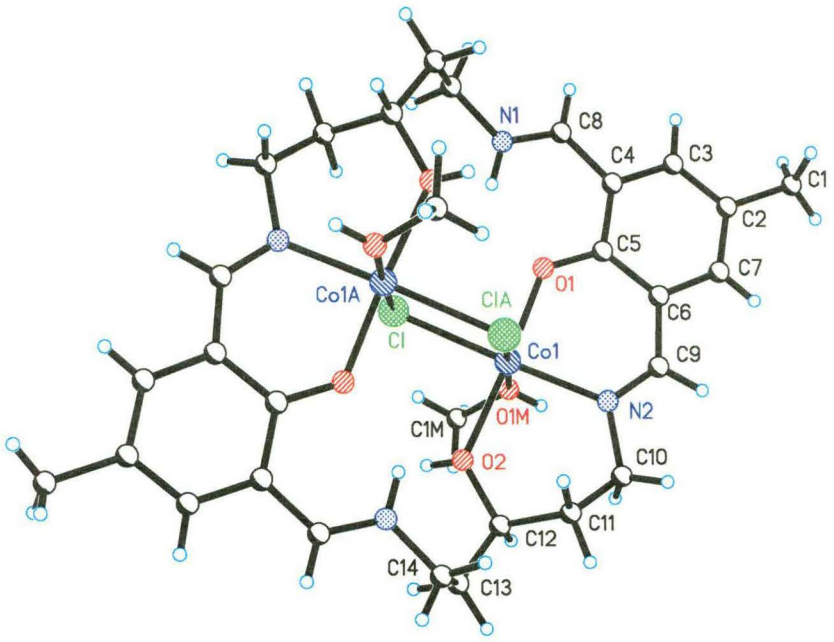


Figure 5·18 : The $[Co_2(H_4LV5)Cl_2(CH_3OH)_2]^{2+}$ cation of complex 40

The molecule has a centre of symmetry with there being half a macrocycle, a chloride ion and a solvent methanol molecule in the asymmetric unit ; two of which are shown in Figure 5·19.

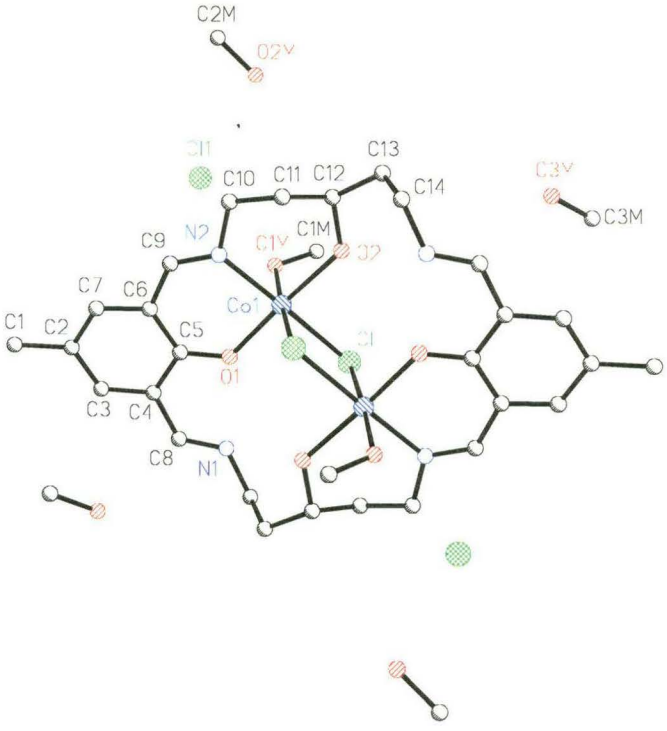


Figure 5·19

The packing diagrams (Figures 5·20, 5·21 and 5·22) reveal that the macrocycles are arranged in rows with a phenol ring of one overlapping the phenol ring of the next. The distance between two adjacent rings is 3·37 Å indicative of π - π interactions. Chloride ions are found between these rows and each chloride ion forms three weak hydrogen bonds. The first of these is to a coordinated methanol group in the macrocyclic complex (Cl1 - O1M - 3·112 Å) and the others are to two methanol solvent molecules one in the same molecule (Cl1 - O2M - 3·124 Å) and one in an adjacent molecule (Cl1 - O3M - 3·189 Å). One methanol molecule is more strongly hydrogen bonded to an alcohol oxygen in an adjacent macrocycle (O2M - O2 - 2·693 Å).

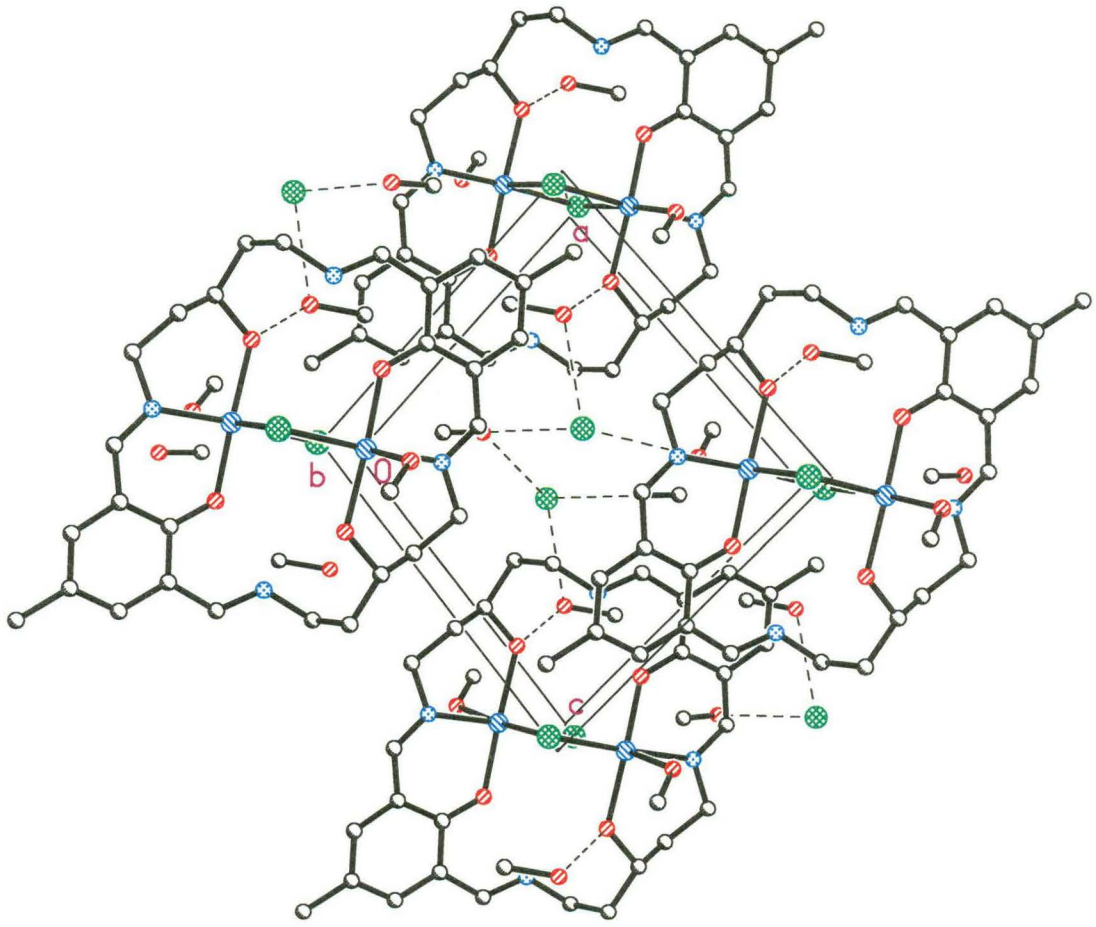


Figure 5·20

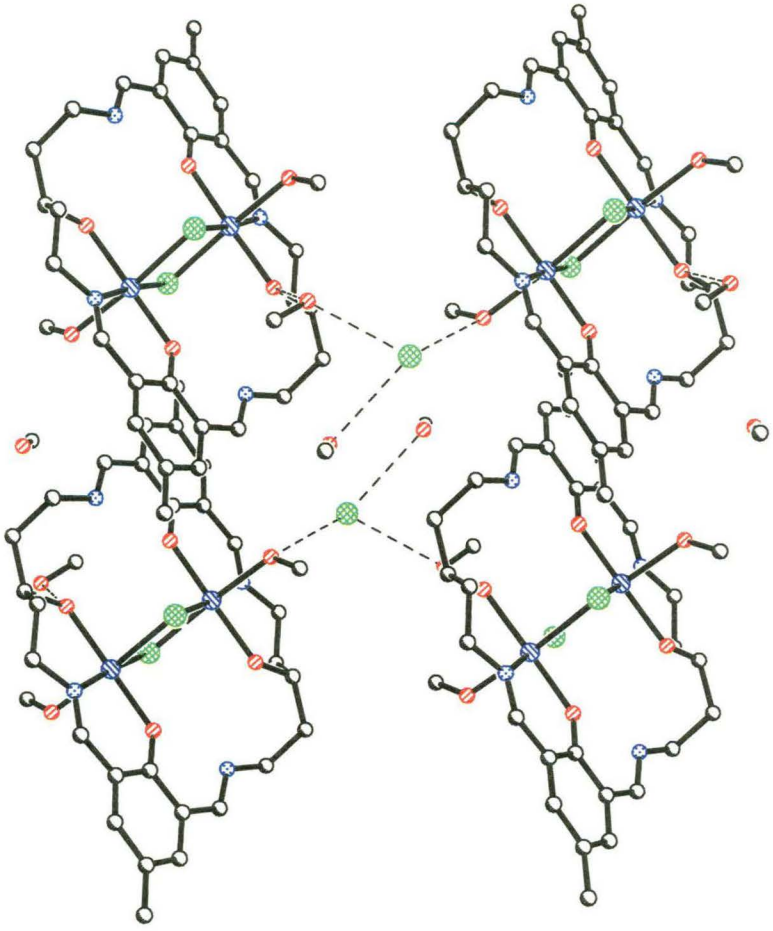


Figure 5·21

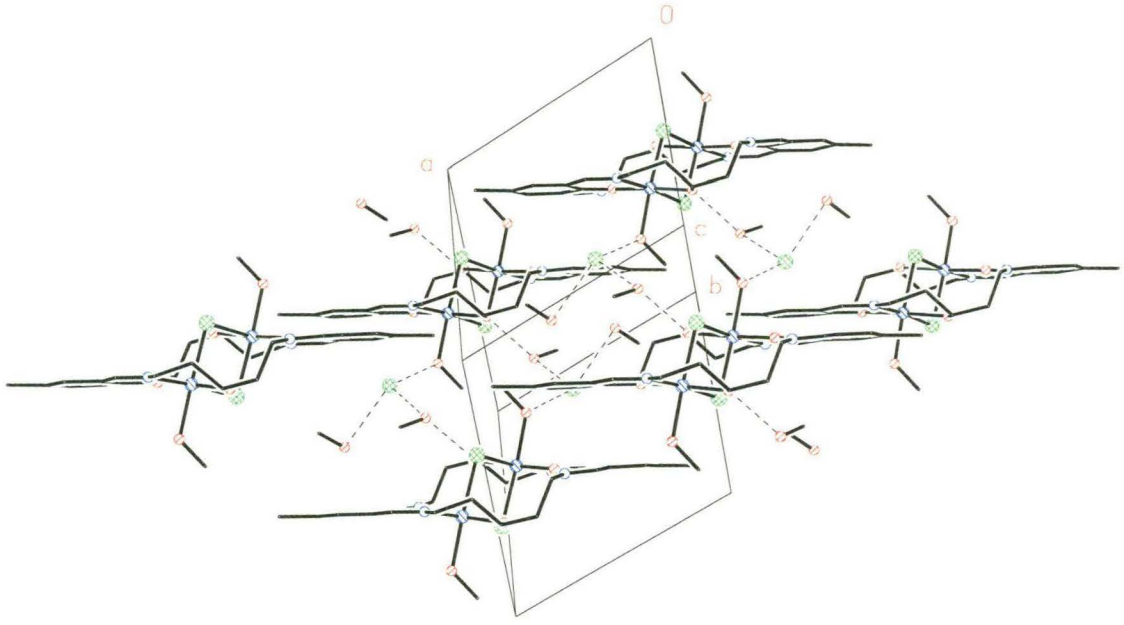


Figure 5·22

Table 5·8 : Selected bond lengths [Å] $[Co_2(H_4LV5)Cl_2(CH_3OH)_2]\cdot 2Cl\cdot 2CH_3OH$

Co(1)-O(1)	2·012(2)	Co(1)-N(2)	2·106(2)
Co(1)-O(2)	2·119(2)	Co(1)-Cl	2·4704(8)

Table 5·9 : Selected bond angles [deg] $[Co_2(H_4LV5)Cl_2(CH_3OH)_2]\cdot 2Cl\cdot 2CH_3OH$

O(1)-Co(1)-O(2)	175·73(6)	O(1)-Co(1)-N(2)	89·61(7)
N(2)-Co(1)-O(2)	94·02(7)	O(1)-Co(1)-Cl	87·35(5)
N(2)-Co(1)-Cl	174·90(5)	O(2)-Co(1)-Cl	88·87(5)
O(1M)-Co(1)-Cl	92·42(5)	C(5)-O(1)-Co(1)	129·63(13)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z

Complex **40** was used for both the magnetic and electrochemical investigation of the binuclear complexes. It was epr silent in DMF. The magnetic moment showed some temperature dependence with the total magnetic moment for the system falling from 5·03 μ_B at 292·1 K to 4·86 μ_B at 80·3 K. This has been calculated to give $2J = -3$ cm^{-1} indicating very weak antiferro-magnetism.

The electrochemical studies were carried out in both CH_3CN and DMF. There were numerous repetitions at different scan rates, and different current and potential ranges. The best of these are reported. Very little change was observed upon changing the scan rate but big changes were observed on going from CH_3CN to DMF. Glassy carbon was used as the working electrode and Pt wire as the counter electrode. The reference electrode was Ag/AgCl and all potentials are quoted with respect to this Ag/AgCl couple. The supporting electrolyte in CH_3CN was tetraethyl-ammonium perchlorate, and in tetrabutylammonium perchlorate. In CH_3CN one irreversible reduction wave (A) with E_c = 1145 mV is seen (Fig. 5·23). It appears that both the Co centres are reduced at the same potential {[Co(II)Co(II)] → [Co(I)Co(I)]}. No oxidation waves are seen even at potentials up to +1200 mV.

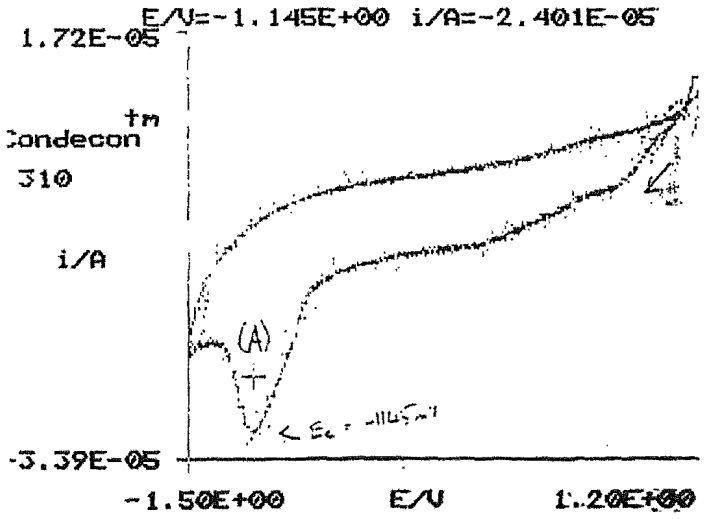


Figure 5·23

Three voltammograms in DMF are shown. In the first (Fig 5·24) a full scan over the range +1250 to -1800 mV is shown and two irreversible reduction waves **B** and **C** and a broad irreversible oxidation wave **D** are seen.

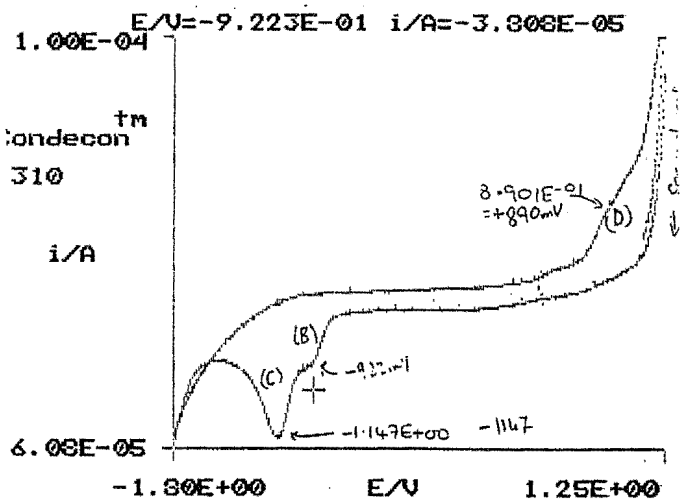


Figure 5·24

The voltammogram between 0 and +1250 mV (Fig. 5·25) shows the irreversible oxidation wave **D** at E_a = +868 mV while in the one recorded between -350 and -1700 mV (Fig. 5·26) the two irreversible reduction waves, **B** and **C**, are seen at E_c = -958 mV and E_c = -1151 mV. This has been interpreted as seeing two **separate** one electron reductions {[Co(II)Co(II)] → [Co(II)Co(I)] → [Co(I)Co(I)]} and a broad ill-defined two electron oxidation [2Co(II) → 2Co(III)].

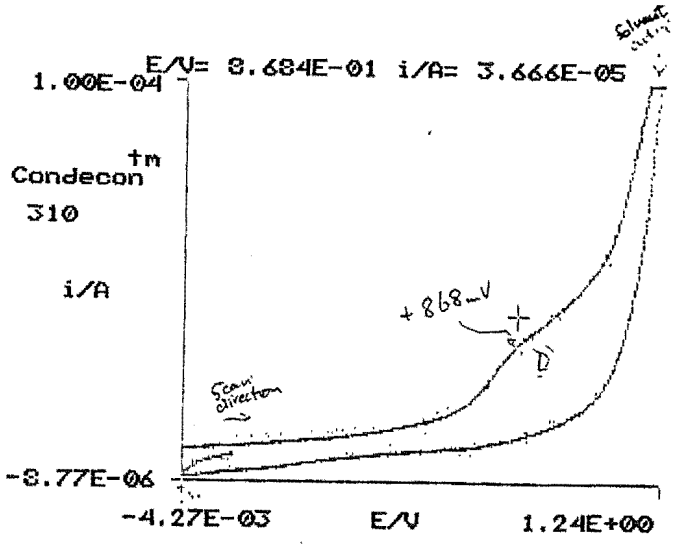


Figure 5·25

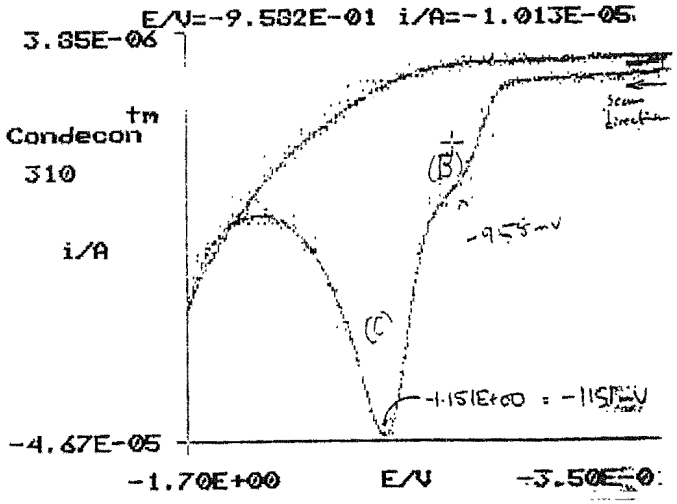


Figure 5·26

It might have been expected that, as the two metal centres are structurally equivalent, a single two electron reduction wave for the simultaneous one-electron reduction of each metal, would have been observed. However, it does appear that two distinct and consecutive one-electron reductions of the bimetallic core are being observed. M^{c}Cann has recently observed this behaviour in one of his dicopper(II,II) complexes which has structurally equivalent metal centres that are reduced at quite separate potentials[226]. In this cobalt complex the two cathodic potentials are only separated by 225 mV which indicates that it would be difficult to isolate the mixed-valence [Co(I)Co(II)] species of this complex. It could also be interpreted that in CH_3CN the bimetallic structure stays intact and both the metals are reduced

simultaneously; whereas in DMF it might be that on dissolution in the solvent the coordination environment of one of the metal centres changes and thus a reduction wave for each of the distinctive metal centres is now seen.

Half of the filtrate of the binuclear complex **40** was treated with NaSCN and from this a green-black microcrystalline material was isolated. The formula **41** $[Co_2$**Lo-s**$Cl_2(NCS)_2]\cdot EtOH\cdot 0\cdot 5H_2O$, an open-sided complex, is proposed for this. The ion $[Co_2$**Lo-s**$Cl_2(NCS)_2]H^+$ is the parent in the FAB-ms.

To check the reproducibilty of the formation of complex **40** a second preparation, using cobalt chloride and **LV5**, was undertaken. It produced six products the first of which appeared as a deep green crust, complex **42**, around the solvent line of the reaction solution. The rest were a succession of powders collected every few days from the filtrates that were sequentially set aside for slow evaporation. These were, in turn, bright yellow complex **43**, lime green (**43a**), green (**43b**) and dark green(**43c**). Finally the frits, that had been used to collect the last two products, were washed with DMF and the resulting brilliant deep green solution set up for ether diffusion. Deep green crystals formed and X-ray analysis of these revealed them to be have the same binuclear core as the previous complexes but with DMF molecules coordinated to the cobalt ions. A $CoCl_4^{2-}$ anion, a disordered DMF molecule and a water molecule complete the structure. The cationic core of complex **44** $[Co_2(H_4$**LV5**$)Cl_2(DMF)_2]$ $CoCl_4^{2-}$ $\cdot DMF\cdot H_2O$ is shown in Figure 5·27.

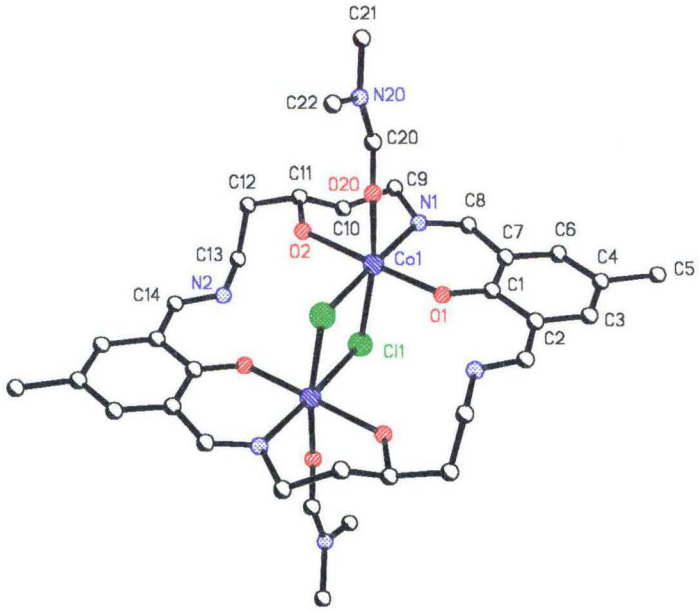


Figure 5·27

Details of the structure showing the $CoCl_4^{2-}$, and the disordered DMF molecule are shown in Figure 5·28.

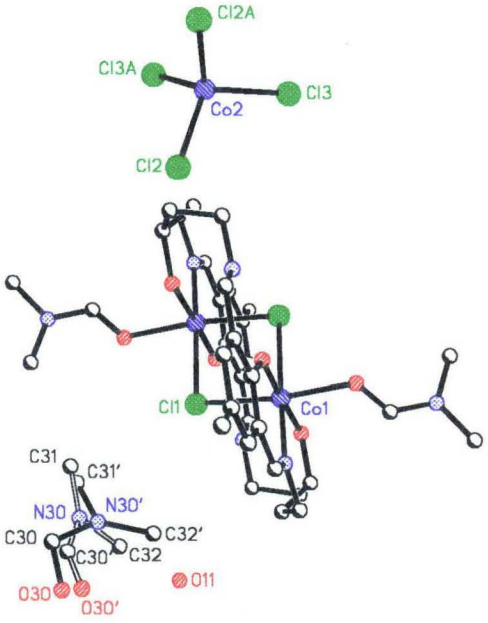


Figure 5·28

In the packing diagrams (Figs. 5·29 and 5·30) it can be seen that the macrocyclic cations are arranged in rows with the $CoCl_4^{2-}$ anions, the water molecules and the solvent DMF molecules found between these rows.

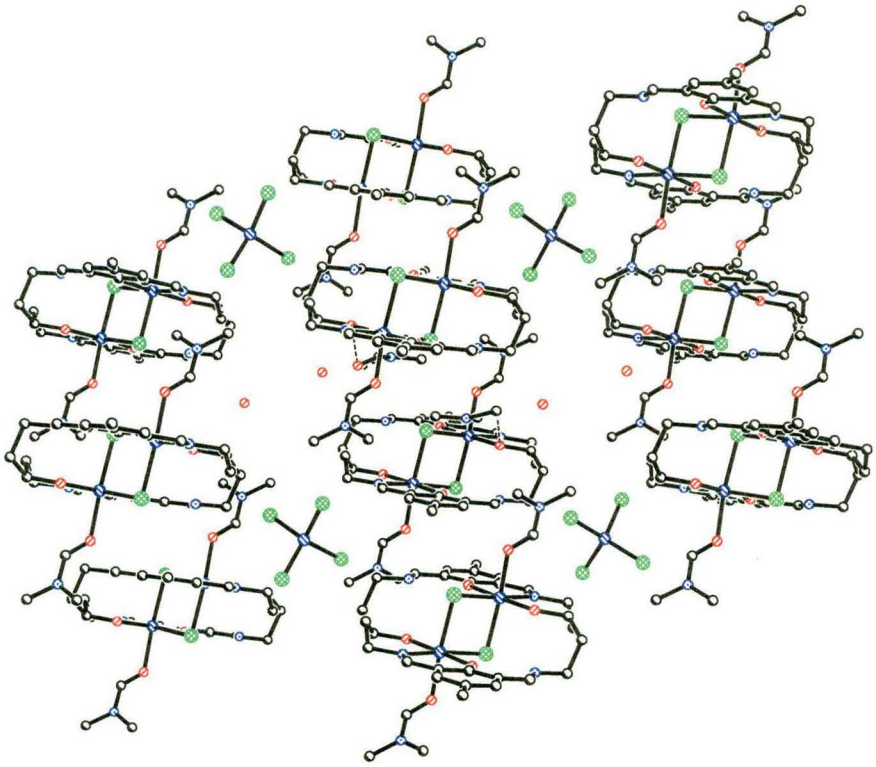


Figure 5·29

Figure 5·30 shows the hydrogen bonding interactions found between the uncoordinated DMF molecules and the alcohol oxygens of the macrocyclic cations.

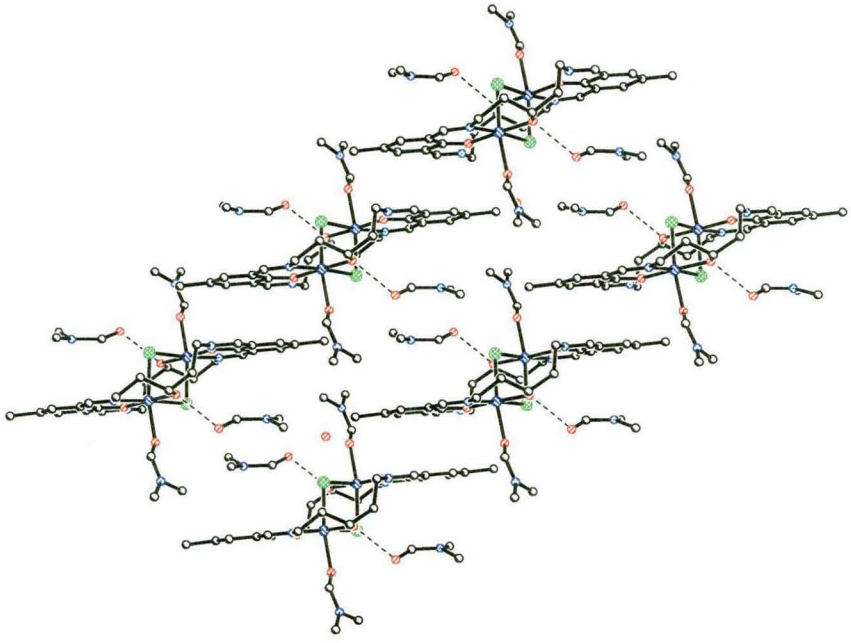


Figure 5·30

Table 5·10 : Selected bond lengths [Å] $Co_2(H_4LV5)Cl_2(CH_3OH)_2]\cdot 2Cl\cdot 2CH_3OH$

Co(1)-O(1)	1·999(5)	Co(1)-N(1)	2·109(6)
Co(1)-O(20)	2·121(6)	Co(1)-O(2)	2·122(5)
Co(1)-Cl(1)	2·50(2)	Co(2)-Cl(2)	2·271(2)
Co(2)-Cl(3)	2·281(2)		

Table 5·11 : Selected bond angles [deg] $[Co_2(H_4LV5)Cl_2(CH_3OH)_2]\cdot 2Cl\cdot 2CH_3OH$

O(1)-Co(1)-N(1)	89·4(2)	O(1)-Co(1)-O(20)	92·4(2)
N(1)-Co(1)-O(20)	92·4(3)	O(1)-Co(1)-O(2)	178·3(2)
N(1)-Co(1)-O(2)	91·3(2)	O(20)-Co(1)-O(2)	86·0(2)
O(1)-Co(1)-Cl(1)	91·1(2)	N(1)-Co(1)-Cl(1)	97·4(2)
O(20)-Co(1)-Cl(1)	169·6(2)	O(2)-Co(1)-Cl(1)	90·3(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+1/2,-z+1 #2 -x,y,-z+3/2

The described preparation using cobalt chloride was repeated a number of times and many variations were made to it. These included using only two metal equivalents, doing the reaction in dry EtOH only, and adding TEA. The highest yields of binuclear products came from the standard reaction mixture. It was noted that overall the yields from the syntheses in which cobalt chloride was the templating salt were considerably better than those in which the perchlorate salt was used* . Complexes **45**, **46**, **47**, were isolated from reaction mixtures in which only MeOH was used as solvent whereas **45** was recovered from a synthesis in which only EtOH was used. Details of the preparations can be found in the experimental section. The crystals of complex **40** $[Co_2(H_4\mathbf{LV5})Cl_2(CH_3OH)_2]$ $2Cl\cdot 2CH_3OH$ were golden whereas those of **44** $[Co_2(H_4\mathbf{LV5})Cl_2(DMF)_2]\cdot CoCl_4^{2-}\cdot DMF\cdot H_2O$ were bright green. All the non-crystalline products were isolated as yellow or green powders. Chemical analyses and the mass spectra (Table 5·13) support the formulation of most of these as binuclear complexes containing chloride anions and a variety of water and/or other solvent molecules.

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* The average yield for the chloride salt is 39 % compared to 21 % for the perchlorate salt.

The proposed formulae for the cobalt chloride complexes not characterised by X-ray crystal structure analysis are shown in Table 5·12.

Table 5·12 : Non-crystalline chloride complexes of LV5

41	$[Co_2$**Lo-s**$Cl_2(NCS)_2]\cdot CH_3CH_2OH$
42, 43, 43a, 43b	$[Co_2(H_4$**LV5**$)Cl_2(H_2O)_2]\cdot 2Cl\cdot nS$ $S = H_2O, CH_3OH, CH_3CH_2OH$
45, 46, 47	$[Co_2(H_4$**LV5**$)Cl_2(H_2O)_2]\cdot 2Cl\cdot nH_2O$ $n = 4$ or 5
48	$[Co_2(H_4$**LV5**$)Cl_2(H_2O)_2]\cdot CoCl_4^{2-}\cdot 4H_2O\cdot CH_3OH$

Table 5·13 : Selected FAB-ms ions of the LV5 - cobalt chloride complexes

		41	**42**	**43**	**43a**	**43b**	**43c**	**44**	**45**	**46**	**47**	**48**
$Co_2(H_4$**LV5**$)Cl_3$	715						715		715			717
Co_2**Lo-s**$(NCS)_2Cl_2H$	714·2	714·2										
$Co_2(H_2$**LV5**$)Cl_2$	679		679	679	679	679	679	679	679	679	680	679
$Co_2(H_2$**LV5**$)Cl$	643		643	643	643	643	643	643	643	643	643	643
Co_2**LV5**	606			606	607	607	607	607	607	606	606	607
$Co(H_4$**LV5**$)Cl$	584	584·0										
$Co_2(H_2$**Lo-s**$)Cl$	562	561·0				561	568					
$Co(H_3$**LV5**$)$	550			550	550			550	550	550	552	550
$Co_2(H_2$**Lo-s**$)$	527	527·1										
$Co\ (H_2$**Lo-s**$)Cl$	504					504	506					
H_4**LV5**	492	490·1										493
$Co(H_2$**Lo-s**$)$		468				468	468					

The reason for the differing colours of the products is thought to be because of the different counter ions as, in all of them, the cationic part appears to be conserved. Occasionally the $CoCl_4^{2-}$ anion is present and in this case the product is always green. However, not all green products contain this anion and the powders have also been observed to change colour from yellow to green while under vacuum filtration or on dissolving in some solvents. A

possible reason for this is the removal of coordinated solvent molecules and their replacement with water or other substitutes. It is thought that the green crystals, which initially formed in the CH_3CN solution of the original perchlorate complex, were a variation of that complex in which CH_3CN was coordinated in place of the water molecules found in the golden crystals which subsequently formed in the same solution.

4 : THE THIOCYANATE COMPLEXES

As well as adding thiocyanate ions to syntheses which were carried out with other cobalt salts, reactions were carried out in which thiocyanate was the only anion added. Cobalt thiocyanate was prepared by the method described in the Experimental section of Chapter 2[209b]. It was expected that chloride ions released from the salt of the diamine would also be present.

A total of six preparations was tried and all the products were green powders or microcrystalline materials. Eight complexes have been identified with six of these being binuclear. The yields were very high (70 - 96 %) indicating the insolubility of the products and this proved to be a problem when trying to run mass spectra of them. However chemical analyses were easy to interpret and the reproducibility of them indicated that these products were quite homogenous. The low solubility of the thiocyanate complexes also meant that lengthening the refluxing time made no appreciable difference to the amount of product isolated. The binuclear complexes have been assigned the following structures (Table 5·14). All attempts to obtain crystals of these complexes have been unsuccessful.

Table 5·14 : Thiocyanate complexes of LV5 and LV5t

49, 50, 51	$[Co_2(H_4\mathbf{LV5})Cl_2(NCS)_3]\cdot nS$ n = 1·5 or 2 S = H_2O or CH_3OH
52	$[Co_2(H_4\mathbf{LV5})Cl_2(NCS)_2]\cdot 1{\cdot}5H_2O\cdot 2CH_3OH$
53, 54	$[Co_2(H_4\mathbf{LV5t})Cl_2(NCS)_3]\cdot nH_2O$ n = 1·5 or 2

5 : THE NITRATE COMPLEXES

55	$[Co_2(H_4\mathbf{LV5})Cl_2(NO_3)_2]\cdot H_2O$

The complexes made with cobalt nitrate have been the most difficult to characterise. It would appear that when the anion used is nitrate, both binuclear and tetranuclear complexes form. Again, with no crystal structures of nitrate complexes available for comparison, sporting techniques have had to be used to elucidate the probable formulae of the products isolated.

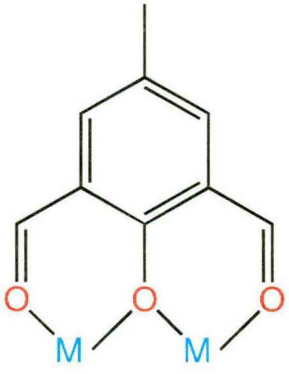
The first **LV5**-nitrate complex isolated is a good example of the difficulties encountered in identifying these products. The product was a fine bright orange powder and showed the distinctive "binuclear" pattern in the IR. The analysis gave very good agreement for the trinuclear complex $[Co_3(H_2\mathbf{LV5})Cl(NO_3)_3]\cdot 2H_2O$. However, the parent and next ion in the FAB-ms were for a binuclear compound (as indicated by the IR) and the base peak was for an open-sided complex containing one cobalt. It is not thought that complexes of this ligand system containing three metal centres exist and the analysis is best explained by a homogenous mixture of a binuclear macrocyclic complex and a complex of the open-sided ligand.

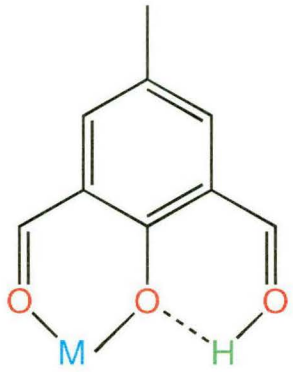
A repeat of this synthesis resulted in a tetranuclear product which has been discussed in Chapter 4. When this preparation was tried a further time an orange-brown microcrystalline material, which the IR indicated was a binuclear complex, was isolated. This has been assigned the formula **55** $[Co_2(H_4\mathbf{LV5})Cl_2(NO_3)_2]\cdot H_2O$.

6 : CONCLUSION

In the course of this work new binuclear macrocyclic complexes, in which the two cobalt ions are diagonally opposed and bridged by chloride ions, have been isolated and characterised. These complexes are stepped and it would seem that this arrangement accommodates the preferred octahedral coordination around the cobalt ions. It is interesting to speculate as to why these particular complexes formed and as to why the chloride bridges are diagonally opposed. The **LV5** ligand system is labile as is cobalt(II) and it is likely that competing reactions are occurring all the time in the formation of the complexes. For example, for the metals to coordinate there is always going to be competiton between the metals and the protons for the ligand donor sites. Under varying conditions one of the competing reactions will dominate and trying to elucidate exactly what is happening is part of the fascination of this study. The system forms tetranuclear complexes as discussed and there is no doubt that many of the products from the different syntheses are mixtures.

It has been proposed, earlier in this work, that in the intial reaction mixture the metals bind to the phenols as shown in Figure 5·30a but as just mentioned this process is competing with the binding of the proton in this site (Fig 5·30b).





Figures **5·30a** **5·30b**

Certainly this competition is demonstrated in the binuclear macrocyclic complexes where the proton is found bound to the imine in the site which could potentially bind another metal (Fig. 5·31).

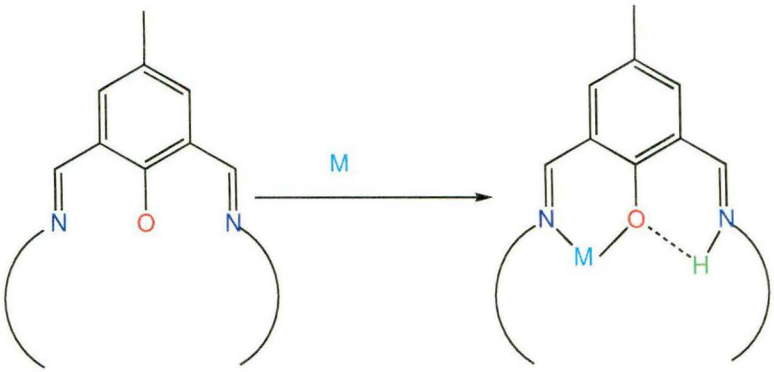


Figure 5·31

It would appear that once a chloride ion has coordinated to cobalt it could bridge to a cobalt oppositely placed but would be too bulky to bridge to a laterally placed one. The twisting of the ligand system to allow octahedral coordination around the cobalt and the coordination of a proton to the imine would then negate the inclusion of two more cobalt ions in the empty sites. That is not to say that these sites are not filled at any time but in solution the processes of coordination are likely to be dynamic whereas in the crystal one or two forms are found. The disorder of the coordination of the cobalt ions, shown by the binuclear complexes supports this idea.

A binuclear copper macrocyclic complex, in which the two metal ions are laterally coordinated (Fig. 5·32), has been made with the **LV5** ligand system[204d]. However in this complex the sytem is planar and the bridging ligand is a much smaller hydroxy group.

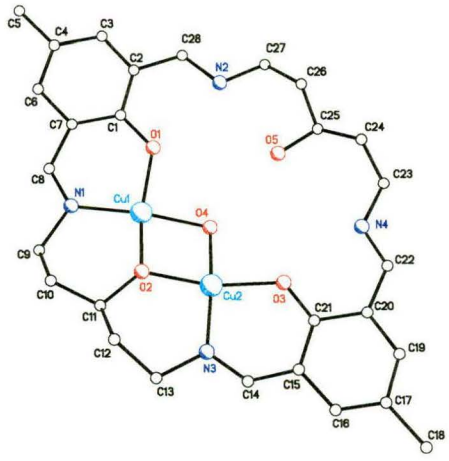


Figure 5·32 : The macrocyclic complex M18 [Cu_2(μ-OH)(HLV5)]

These binuclear complexes offer exciting routes into heterotetranuclear complexes of this ligand system. Oxidation of both cobalt ions to inert Co(III) will allow the addition of other metals in the vacant coordination sites (Fig 5·33) without exchange taking place.

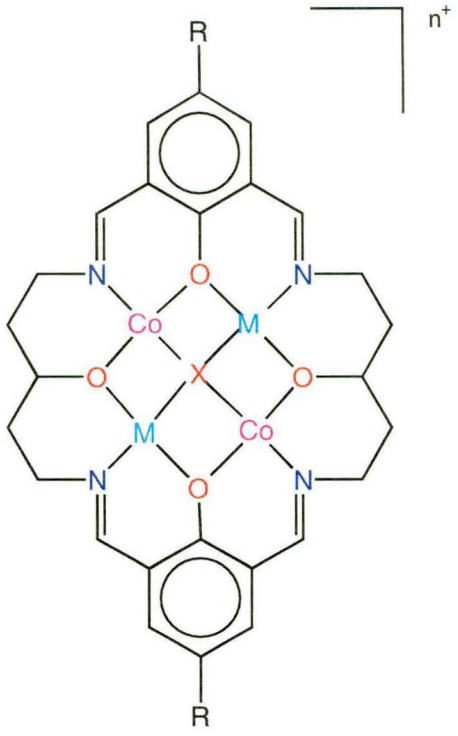


Figure 5·33 : A hetero-tetranuclear complex of LV5

The most simplistic and optimistic approach to this would be to use an agent that would both oxidise the metal and precipitate the chloride ions in a single step reaction. Addition of stoichiometric amounts of a silver salt could be one way of achieving this. The preferred silver salt would be the perchlorate as it has only weakly coordinating anions. Preliminary work on this has been done. Complex **46** $[Co_2(H_4\mathbf{LV5})Cl_2(H_2O)_2]\cdot 2Cl\cdot 4H_2O$ was dissolved in DMF to form a golden brown solution and six equivalents of silver nitrate were added. It was hoped that two equivalents would oxidise both of the Co(II) ions to Co(III) and that the other four would precipitate the chloride ions. On addition of the silver salt a precipitate was formed and after some stirring the mixture was filtered by dripping it slowly through a pipette packed with glass wool. This was repeated until no more precipitation took place when it was finally filtered into a stirring solution containing two equvalents of copper nitrate. This was chosen as it contains the same anion as in the silver salt. The bright green copper solution

instantly changed to a khaki colour on addition of the cobalt solution. The combined mixture was allowed to sit for a few hours, it was filtered and then set aside for crystallisation.

Another approach to the oxidation of these complexes might be to use molecular bromine as Robson did with his binuclear cobalt macrocycles[100].

There is much more work to be done with the cobalt complexes of **LV5** and **LV5t**. This includes finding efficient ways of separating the mixtures that result from many of the syntheses. The binuclear complexes will be exploited as routes into heterobinuclear compounds. Experimentation with methods of crystallisation of all of the products in a hope of verifying the postulated formulae for these will continue to be a challenge.

EXPERIMENTAL

3 : COBALT WITH PERCHLORATE

LV5 Complexes

Complex 31 : $[Co_2(H_4LV5)Cl_2(H_2O)_2]\cdot 2ClO_4\cdot 2CH_3CH_2OH$.

Complex 34 : $[Co_2(H_4LV5)Cl_2(ClO_4)_2]\cdot H_2O + 8CoCl_2$

Complex 35 : $[Co_2(H_4LV5)Cl_2(ClO_4)_2]$

Complex 36 : $[Co_2(H_2Lo\text{-}s)Cl_2(ClO_4)_2]$

DMFP (0·324 g, 2 mmol) and $CoClO_4$ (1·464 g, 4 mmol) were dissolved in ~ 40mL dry MeOH and the resulting golden brown solution refluxed 10 mins. DAHP.Cl_2 (0·382 g, 2 mmol) was dissolved with heating and stirring in ~ 20 mL of dry MeOH, KOH solution (0·224 g, 4 mmol) was added and the resulting solution sat in ice the KCl precipitated. On addition of the DAHP solution the refluxing mixture became a dark brown solution which was refluxed 66 h. The reaction mixture was cooled to ambient temperature and stood ~ 6h at which time a solid was visible. This pale yellow brown powder **34** was collected by vacuum filtration and washed with dry EtOH.

Yield : 0·31 g, 0·161 mmol, 16·1 %

IR : 3478, 3195, 2923, 1654, ~1630sh, 1546, 1357, 1088, 867, 816, 777, 626 cm^{-1}

FAB-ms ($^m/_e$) : 934(2), 859(2), 781(12), 707(11), 679(33), 643(100), 607(12), 550(16)

UV (DMF) : 654, 587sh, 414

Analysis for : $[Co_2(H_4\mathbf{LV5})Cl_2]\cdot 2ClO_4\cdot H_2O + 8CoCl_2$

Calculated :	C : 17·38;	H : 1·88;	N : 2·90 %
Found :	C : 17·46;	1·84;	2·96 %

The filtrate was set aside and eventually dried to a deep orange glassy material. When dry EtOH was added to this some dissolved to form a moss

green solution but most remained solid and was collected, in a frit, as dark brown glassy "chunks" **35** and **36**.

Yield : 0·536 g, 0·298 mmol, 30 %

IR : 3437, 3246, 2926, 1663, 1638, 1537, 1234, 1094, 625 cm^{-1}

FAB-ms ($^{m}/_{e}$) (500↑) : 79?(37), 777(33), 743·1(100), 707·1(90), 643·1(71), 623·9(69), 568·1(75), 540·2(100), 525·1(78).

FAB-ms ($^{m}/_{e}$) (200↑) : 743·1(8), 707·1(8), 643·1(11), 623·9(9), 568·1(5), 540·2(18), 525·1(11), 467·1(100).

FAB-ms ($^{m}/_{e}$) : 979·2(), 952·1(), 875·9(), 777·1(), 743·1, 707·1(), 643·1(), 623·1(), 606(), 568·1(), 525·1(), 483·1() 467·1(100),

777·0 : H_2**LV5** + 2Co + 2Cl + ClO_4
743·1 : H_2**LV5** + 2Co + Cl + ClO_4 + H^+
623·9 : H_2**Lo-s** + 2Co + ClO_4
568·1 : H_2**Lo-s** + Co + ClO_4
525·1 : H_2**Lo-s** + 2Co
467·1 : H_2**Lo-s** + Co

Approximately half the peaks identified in the mass spectrum were for the open-sided complex and half for the full ligands.

Complex 36 : [Co_2(H_2Lo-s)Cl_2(ClO_4)$_2$]

Calculations for the analysis for binuclear, trinuclear or tetranuclear complexes of **LV5** were always high in N_2. The IR has features found in the tetranuclear and binuclear complexes. When a calculation was done for a 50 : 50 mix of binuclear full and open-sided complexes (based on complexes **35** [Co_2(H_4**LV5**)Cl_2(ClO_4)$_2$] and **36** [Co_2(H_2**Lo-s**)Cl_2(ClO_4)$_2$]) it was very close to that found.

Analysis for :

{0·5[Co_2(H_4**LV5**)Cl_2(ClO_4)$_2$] + 0·5[Co_2(H_2**Lo-s**)Cl_2(ClO_4)$_2$]}·2·5H_2O·MeOH

Calculated :	C : 37·39;	H : 3·90;	N : 5·08 %
Found :	C : 37·32;	H : 3·99;	N : 5·03 %

UV (DMF) : 415, 361

Under vacuum the green filtrate became a dark brown colour. After five weeks tiny orange crystals **31** suitable for single crystal X-ray diffraction studies were visible in this filtrate.

Complex 31 $[Co_2(H_4LV5)Cl_2(H_2O)_2]\cdot 2ClO_4\cdot 2CH_3CH_2OH$. The crystal structure revealed first of the diagonally chloride-bridged cobalt structures with perchlorate anions.

Complex 32 : $[Co_2(H_4LV5)Cl_2(CH_3OH)_2]\cdot 2ClO_4\cdot H_2O\cdot 2CH_3OH$

DMFP (0·324 g, 2 mmol) and $CoClO_4$ (1·464 g, 4 mmol) were dissolved in dry MeOH (~ 40mL) and the resulting golden brown solution refluxed 15 mins. DAHP.Cl_2 (0·382 g, 2 mmol) was dissolved with heating and stirring in ~ 20 mL of dry MeOH and 20 mL preprepared KOH (0·224 g, 4 mmol) added and the resulting solution sat in ice for ~ 2 h to precipitate the KCl. The DAHP solution was added to the refluxing mixture dropwise by filtering through a paper at the top of the condenser. The resulting golden brown solution was refluxed 62.5 h after which time a small amount of white powder (IR ⇒ it is inorganic - probably KCl) was collected.

The golden brown filtrate was set aside and within 3 days red-orange crystals **32** were visible in this filtrate. It took three recrystallisations to get a crystal good enough to collect a data set and this investigation showed the complex to be $[Co_2(H_4\mathbf{LV5})Cl_2(CH_3OH)_2]\cdot 2ClO_4\cdot H_2O\cdot 2CH_3OH$. This structure was essentially the same as the previous macrocycle but with different solvent molecules. However, it was disordered with 48% one orientation and 52% the other.

IR : 3482, 2922, 1641, 1546, 1356, 1232, 1089, 864, 816, 776, 624 cm^{-1}

ES - ms ($^m/_e$) (5·61e7) : 799·4(2), 753·4(9), 650·5(9), 593·6(100), 586·5(13), 493·6(42), 474·6(12).

When some of these crystals were removed by pipette and dissolved in CH_3CN square green crystals formed first followed by golden oblong ones the same as the originals. When these crystals were left exposed to the air they became a yellow powder.

Complex 33 : $[Co_2(H_4LV5)Cl_2(ClO_4)_2]\cdot H_2O\cdot CH_3CH_2OH$

The dahp solution was prepared as for 704·1. DMFP (0·324 g, 2 mmol) and $CoClO_4$ (1·464 g, 4 mmol) were mixed in ~ 40mL dry MeOH and the resulting golden solution refluxed 35 mins. The DAHP solution was added to the refluxing mixture dropwise by filtering through a paper at the top of the condenser. The resulting golden brown solution was refluxed 69 h after which time a small amount of white powder (IR indicated this was KCl) was collected by vacuum filtration. The brown filtrate was set aside and within 2 days red-orange crystals **33** suitable for single crystal X-ray diffraction studies were visible in this filtrate. The dried filtrate of these crystals was scraped into a vial, taken to Belfast and redissolved in MeOH. Not all of it dissolved and the yellow powder residue (0·085 g) was collected. The remaining solution was set up for ether diffusion.

IR : 3447, 3254, 3049, 2924, 1655, 1635(sh), 1545, 1232, 1096, 991, 868, 816, 777, 718, 623 cm^{-1}

FAB-ms ($^m/_e$) : 1185(5), 1166(6), 866(10), 828(2), 568(38), 525(10), 468(100)

866 = **LV5** + 4Co = 4Cl
468 = H_2**Lo-s** + Co

Chemical analysis suggests this is a mixture of the open-sided and a tetranuclear ligand. After eleven days the solution in ether contained crystals around the solvent line and in a clump at the bottom of the vial. As a cell check showed these to be the same as the original **33** crystals they were used for analysis and IR.

IR : 3429, 2924, 2868, 1655, 1541, 1232, 1094, 868, 816, 777, 625 cm^{-1}

FAB-ms ($^m/_e$) : 743(30), 707(17), 679(17), 643(100), 607(28), 550(25).

Base peak = H_2**LV5** + 2Co + Cl

Parent ion = H_2**LV5** + 2Co + 2Cl + ClO_4 + H

Analysis for : $[Co_2(H_4LV5)Cl_2(ClO_4)_2]\cdot H_2O\cdot CH_3CH_2OH$

Calculated :	C : 38·89;	H : 4·89;	N : 5·67 %
Found :	C : 38·69;	H : 4·89;	N : 5·74 %

Complex 37 : $[Co_2(H_4LV5)Cl_2(H_2O)_2]\cdot 2ClO_4\cdot 2CH_3CH_2OH\cdot 2H_2O$

The dahpCl_2 was stirred in 30 mL warm dry EtOH but didn't dissolve until some MeOH was added. The $Co(ClO_4)_2$ and dfmp dissolved in dry EtOH to form a golden solution which was refluxed for 15 mins before the dahp was added. The reaction mixture was refluxed 120 h. After this time the only visible solid was a small amount of yellow powder coating the magnetic stirrer. The reaction mixture was filtered hot and set aside for slow evaporation. After a few days masses of golden crystals **37** were evident in this solution.

IR : 3417, 2924, 1655, 1630(sh), 1355, 1233(2 spl), 1120(sh), 1100, 875, 822, 783, 635 cm^{-1}

ES-ms ($^m/_e$) : 752(12), 678(19), 650(10), 593(100), 550(10), 493(76).

UV : sh588, 415

Analysis for : $[Co_2(H_4\mathbf{LV5})Cl_2(H_2O)_2]\cdot 2ClO_4\cdot 2CH_3CH_2OH\cdot 2H_2O$

Calculated :	C : 36·87;	H : 5·22;	N : 5·37 %
Found :	C : 36·97;	H : 5·18;	N : 5·50 %

Complex 38 : $[Co_2(HLo\text{-}s)(ClO_4)_{1.5}Cl_{0.5}]\cdot 4H_2O\cdot CH_3CH_2OH$

$Co(ClO_4)_2$ (1·464 g, 4 mmol) was dissolved in ~ 20 mL dry MeOH and brought to reflux. DMFP (0·324 g, 2 mmol) was separately dissolved in ~ 20 mL dry MeOH and added to the metal salt. The resulting golden brown solution was refluxed 10 mins. DAHP.Cl_2 (0·82 g, 2 mmol) was dissolved with heating and stirring in ~ 15 mL of dry MeOH, KOH solution (0·224 g, 4 mmol) was added and the resulting solution sat in ice for 6 h to precipitate the KCl. The mixture became a dark brown solution which was refluxed ~ 15 mins. TEA (0.5 mL ~ 6 mmol) was added dropwise and solid appeared in the mixture almost immediately. After 18 h, as there was already a significant amount of solid evident, the refluxing was stopped. This yellow-brown powder was collected by vacuum filtration and washed with dry EtOH. As this solid was collected more formed in the filtrate. This filtrate was contaminated by water sucking back into it and immediately more solid **38** appeared. This was collected in filter paper.

Yield : 0·123 g, 0·151 mmol, 20 %

IR : 3750, 3441, 2924, 2829, 1632, 1540, 1234, 1109, 898, 838, 768, 725, 624 cm^{-1}

FAB-ms ($^m/_e$) : 600(100), 561(53), 445(90) - not a lot above background.

600 : **Lo-s** + 3Co + O

445 : H_3**Lo-s** + $2H_2O$ + H

Analysis for : $[Co_2(H\textbf{Lo-s})(ClO_4)_{1.5}\ Cl_{0.5}]\cdot 4H_2O\cdot CH_3CH_2OH$

Calculated :	C : 37·01 ;	H : 4·72 ;	N : 3·45 %
Found :	C : 37·02;	H : 4·77;	N : 3·55 %

Complex 39 : $[Co_2(HLo\text{-}s)(ClO_4)Cl]\cdot 4H_2O\cdot 0\cdot 5CH_3CH_2OH$

The filtrate was of **38** set aside for further evaporation and after 15 days more solid **39** (a khaki powder) was collected from this.

Yield : 0·085 g, 0·116 mmol, 12 %

IR : 3429, 2913, 1655(sh), 1630, 1535, 1229, 1115, 1095, 898, 838, 768, 725, 645, 635 cm^{-1}

FAB-ms ($^m/_e$) : 920·8(29), 902·8(37), 891·8(16), 845·8(27), 827·8(31), 790·8(21), 777·8(19), 763·8(33), 652·8(36), 599·8(100), 524·8(38),

Analysis for : $[Co_2(H\textbf{Lo-s})(ClO_4)Cl]\cdot 4H_2O\cdot 0\cdot 5CH_3CH_2OH$

Calculated :	C : 38·11	H : 4·66;	N : 3·70 %
Found :	C : 38·06;	H : 4·63;	N : 3·73 %

2 : COBALT WITH CHLORIDE

LV5 Complexes

Complex 40 : $[Co_2(H_4LV5)Cl_2(CH_3OH)]\cdot 2Cl\cdot 2CH_3OH$

DFMP (0·324 g, 2 mmol) and $CoCl_2$(0·952 g, 4 mmol) were mixed in dry MeOH (20 mL) and the resulting brown solution refluxed ~ 20 mins. DAHP.Cl_2 (0·382 g, 2 mmol) and KOH (0·224 g, 4 mmol) were dissolved separately with heating and stirring in ~ 20 mL of dry MeOH. These solutions were combined and the resulting mixture was sat in ice for ~ 3 h to precipitate the KCl. The DAHP solution was added to the refluxing mixture dropwise by filtering through a paper at the top of the condenser. After refluxing 64 h an inorganic material

was separated from the brown reaction mix which was filtered hot through a sintered glass funnel. The dark brown filtrate was set aside for slow evaporation yielding golden crystals suitable for single crystal X-ray diffraction studies. These crystals lost solvent quickly to form a green powder. X-ray structure analysis of **40** showed this to be a diagonally chloride bridged binuclear cobalt complex with two additional chloride anions.

Complex 41 : $[Co_2(H_4Lo\text{-}s)Cl_2(NCS)_2]\cdot CH_3CH_2OH\cdot 0\cdot 5H_2O$

The filtrate from which **40** had been isolated was halved. One half was treated with LiCl and the other with NaSCN. The latter eventually yielded two lots of a green-black microcrystalline material which were combined as the IRs were identical.

Yield : 0·195 g, 0·250 mmol, 33·37 %

IR : 2080, 1660, 1665, 1630(sh), 1605(sh) 1545, 1234, 1220?, 878, 825, 755, 725 cm^{-1}

FAB-ms ($^m/_e$) : 771·1(3), 714·2(2), 584·0(9), 561·0(9), 527·1(10), 490·1(10), 468(100)

714·2 = **Lo-s** + 2Co + 2Cl + 2NCS + H

468 : H_2**Lo-s** + Co

Analysis - $[Co_2(H_4$**Lo**-s$)Cl_2(NCS)_2]\cdot CH_3CH_2OH\cdot 0\cdot 5H_2O$

Calculated :	C : 42·26 ;	H : 3·94;	N : 7·30 %
Found :	C : 42·27;	H : 4·01;	N : 7·29 %

Complex 42 : $[Co_2(H_4LV5)Cl_2(H_2O)_2]\cdot CoCl_4\cdot 4\cdot 5H_2O\cdot 0\cdot 5CH_3OH$

Complex 43 : $[Co_2(H_4LV5)Cl_2(OH)_2]\cdot Co(OH)_2\cdot 3H_2O\cdot CH_3OH$

Complex 44 : GDMF : $[Co_2(H_4LV5)Cl_2(DMF)_2]\cdot CoCl_4^{2-}\cdot DMF\cdot H_2O$

The procedure which yielded **40** and **41** was repeated. Preprepared KOH and dahpCl_2 solutions were each made with 10 mL MeOH (not dry). These solutions were combined and the resulting mixture was sat in ice for ~ 3 h to precipitate the KCl. The $CoCl_2$ was stirred in hot MeOH for 30 mins and dry dmfp, rinsed with an additional 10 mLs of MeOH, added. The resulting blue solution was refluxed 20 mins before dahp solution was added. After 19 h refluxing the reaction mixture was deep green with a solid crust around the solvent line.

Because this result was different to the previous time the refluxing was stopped and the reaction mixture filtered hot through a sintered glass funnel and the dark green solid **42**, which had to be washed out of the flask with MeOH, collected.
Yield : 0·02 g, 0·02 mmol, 3 %

Addition of MeOH to the filtrate of **42** caused precipitation of a yellow powder **43.** Yield : 0·36 g, 0·403 mmol, 40·3 %

The golden brown filtrate was set aside for slow evaporation and after 2 days 0·05 g of lime green powder **43a** was collected. The golden brown filtrate was left for further evaporation and after a 2 days the walls of the flask were coated with bright green powder. CH_3CN was added and some powder dissolved to form a bright blue solution. The undissolved green solid **43b** (0·053 g) was collected. The filtrate was further evaporated to a sludge from which a dark green powder **43c** (0·33 g) was retrieved.

The frits which had been used to collect **43b** and **43c** were rinsed with dmf and the residues dissolved instantly. The brilliant deep green solution was set up for ether diffusion and yielded crystals **44** suitable for X-ray structure determination. **44** was also a binuclear cobalt complex containing diagonal chlorine bridges but this time incorporating $CoCl_4^{2-}$ anions.

IR

42	1654		1545	1356	1233		897	869	815		
43	1654	1630	1544		1235/28			878	825		
43a	1651	1631	1547	1355	1233	924		868	815		715
43b	1653		1543	1351	1233	995		865	817	769	719
43c	1657		1537	1357	1233	995		871	821	769	719
44	1655	1632	1548	1357	1237			868	815	778	

UV(DMF)

42	not enough					
43	661·6	630·4sh		602·8		416·8
43a	668·4	630sh		603·6	598·8sh	414·8
43b	668·4	630sh		603·6	598·8sh	412
43c	667·6	630·4sh	624·4sh	604	596·8sh	412

UV(CH_3CN)

42	678·0	657·0	625·0sh	586·0	573·0
43	not soluble				
43a	677·6	660·8sh	632·0sh	585·2	572sh
43b	677·6	658·4sh	629·6	585·2	573·2
43c	677·6	656·0sh	629·6	585·2	573·2
44	678·8	656·0sh	624·8sh	585·8	570·8

42

FAB-ms ($^m/_e$) : 870(2), 846(5), 831(3), 798(5), 772(5), 736(26), 679(11), 643(100).

ES-ms ($^m/_e$) : 827·6(1), 649·4(11), 622·5(1), 586·2(2), 550·4(2), 506·2(2), 493·5(5), 448·5(3), 403(2), 304·5(1), 247·4(100).

Analysis for : $[Co_2(H_4\mathbf{LV5})(Cl_2(H_2O)_2]\cdot CoCl_4^{2-}\cdot 4\cdot 5H_2O\cdot 0\cdot 5CH_3OH$

Calculated :	C : 33·78;	H : 4·87;	N : 5·53 %
Found :	C : 33·59;	H : 4·94;	N : 5·50 %

43

FAB-ms ($^m/_e$) : 1284(3), 1249(2), 1192(1), 830(3), 794(1), 736(10), 679(33), 643(100), 606(26), 550(33).

ES-ms ($^m/_e$) : 679(1), 623(1), 586(1), 550(1), 493(5), 304(2), 276(4), 247(100).

Analysis for : $[Co_2(H_4\mathbf{LV5}Cl_2(OH)_2]\cdot Co(OH)_2\cdot 3H_2O\cdot CH_3OH$

Calculated :	C : 39·03;	H : 5·42;	N : 6·28 %
Found :	C : 38·93;	H : 5·59;	N : 6·37 %

43a

FAB-ms ($^m/_e$) : 774(3), 736(17), 679(42), 643(100), 607(22), 550(14).

ES-ms ($^m/_e$) : 1223(1), 1005(1), 729(1), 654(1), 625(1), 586(1), 551(1), 494(4), 467(2), 437(1), 411(1), 325(1), 276(100), 247(100).

43b

FAB-ms ($^m/_e$) : 868(3), 846(6), 828(6), 807(9), 771(12), 736(24), 679(42), 643(100), 607(33), 561(24), 504(27), 468(72).

ES-ms ($^{m}/_{e}$) : 1387(1), 1206(1), 1121(1), 1055(1), 751(1), 714(1), 658(2), 638(2), 603(2), 586(2), 505(2), 493(4), 411(4), 358(2) 329(6), 276(9), 248(100).

43c

FAB-ms ($^{m}/_{e}$) : 1075(2), 938(2), 882(3), 844(3), 828(5), 809(6), 771(15), 715(5), 679(5), 643(15), 607(9), 568(11), 506(22), 468(100).

ES-ms ($^{m}/_{e}$) : 714(2), 658(3), 493(5), 411(14), 357(9), 329(8), 265(13), 247(100), 236(42).

44

FAB-ms ($^{m}/_{e}$) : 831(9), 774(5), 736(47), 679(32), 643(100), 607(28), 550(13).

ES-ms ($^{m}/_{e}$) : 493(10), 412(4), 339(10), 295(2), 247(100).

Complex 45 : $[Co_2(H_4LV5)Cl_2(H_2O)_2]2Cl{\cdot}5H_2O$

The procedure was as reported but the $CoCl_2$ and dfmp were mixed in ~ 20 mL of dry MeOH and the brown solution refluxed 15 mins, after which time a green crust had formed around the solvent line. The dahp solution was made from $dahpCl_2$ being dissolved in 20 mL dry MeOH, 20 mL of a fresh KOH solution being added and the lot sat in ice for 70 mins. Initially the reaction mixture was green but after 16 h reaction mix was brown, cooled (fault in the hot-plate stirrer) and contained yellow powder sticking to the flask walls. The mixture was reheated for a further 6 h. The reaction mixture was filtered hot through a sintered glass funnel and the yellow powder collected in a frit and air dried. The brown filtrate was let evaporate slowly and after one week further yellow powder was collected. The IRs of these two products showed them to be the same and they were combined.

Yield : 0·34 g, 0·388 mmol, 38·8 %

IR: 3349, 3248, 3041, 2937, 1665, 1630, 1545, 1354, 1234, 925, 879, 816 cm^{-1}

FAB-ms ($^{m}/_{e}$) : 866(1), 846(2), 828(2), 809(3), 797(4), 771(11), 715(5), 679(57), 643(100), 607(14), 550(40).

ES-ms ($^{m}/_{e}$) : 849(3), 754(5), 689(12), 679(38), 586(48), 550(85), 493(100), 481(5), 375(18), 341(22), 322(38), 276(32), 247(100).

UV(DMF) : 663·2sh, 630·8, 603·2sh, 598·4, 416·4

Analysis for $[Co_2(H_4\mathbf{LV5})Cl_2(H_2O)_2]2Cl{\cdot}5H_2O$

Calculated :	C : 38·37;	H : 5·52;	N : 6·39 %
Found :	C : 38·44;	H : 5·54;	N : 6·36 %

Complex 46 : $[Co_2(H_4LV5)Cl_2(H_2O)_2]\cdot 2Cl\cdot 4H_2O$

Dfmp (2 mmol) and $CoCl_2$ (2 mmol) were mixed in 30 mL dry MeOH and refluxed ~ 20 mins. The solution was brown on mixing but green after refluxing. The dahpCl_2 was dissolved, with heating and stirring in ~ 20 mL of dry MeOH, preprepared KOH solution (4 mmol) added and the resulting mixture sat in ice for ~ 3 h to precipitate the KCl. After the dahp solution was added to the refluxing mixture it formed a brown solution. After two days a small green crust had formed around the solvent line but this redissolved after the flask was swirled After refluxing 66 h some fine yellow brown powder was evident sticking to the flask walls. The reaction mixture was filtered hot through a sintered glass funnel and the yellow powder **46** collected.

Yield 0·33 g, 0·385 mmol, 38·5 %

IR : 3341, 3210, 3086, 2939, 2918, 2858, 1653, 1631, 1547, 1354, 1235, 926, 872, 814.

FAB-ms ($^m/_e$) : 1284(2), 832(2), 797(1), 736(6), 679(42), 643(100), 606(18), 550(27).

ES-ms ($^m/_e$) : 808(1), 738(1·5), 679(1), 643(23), 550(53), 494(37), 322(6), 304(78), 276(18), 247(100).

UV : 663·2, 630·2sh, 603·2, 596sh, 416·8

Analysis for : $[Co_2(H_4\mathbf{LV5})Cl_2(H_2O)_2]\cdot 2Cl\cdot 4H_2O$

Calculated :	C : 40·00;	H : 5·56;	N : 6·44 %
Found :	C : 40·05;	H : 5·48;	N : 6·46 %

Complex 47 : $[Co_2(H_4LV5)Cl_2(H_2O)_2]\cdot 2Cl\cdot 5H_2O$

The yellow brown powder **47** was isolated from the dark brown filtrate of **46** after slow evaporation over 8 weeks.

Yield 0·12 g, 0·137 mmol, 13·7 %

IR : 3360, 3212, 2905, 1655, 1635, 1549, 1356, 1234, 878, 823, 787 cm^{-1}

FAB-ms ($^m/_e$) : 1274(2), 1236(2), 867(1), 825(2), 806(4), 771(4), 733(10), 680(35), 643(100), 606(27), 552.

ES-ms ($^m/_e$) : 689(1), 672(1), 622(1), 586(3), 493(10), 454(1), 378(1), 315(1), 304(3), 276(18), 247(100).

UV : 661·4, 629·6sh, 602·6, 596sh, 416·2

Analysis for : $[Co_2(H_4\mathbf{LV5})Cl_2(H_2O)_2]\cdot 2Cl\cdot 5H_2O$

Calculated :	C : 38·37;	H : 5·52;	N : 6·39 %
Found :	C : 38·40;	H : 5·57;	N : 6·29 %

Complex 48 : $[Co_2(H_4LV5)Cl_2(H_2O)_2].CoCl_4^{2-}\cdot 4H_2O\cdot CH_3OH$

DMFP (2 mmol) and $CoCl_2$ (4 mmol) were mixed in 20mL dry EtOH to form a bright blue solution, and brought to reflux. The heating was turned off for 75 mins (because of a seminar) and then the mixture reheated and refluxed for 15 mins DAHP.Cl_2 (2 mmol) was heated for quite some time in dry EtOH and when it did not dissolve some MeOH was added. 20 mL of KOH solution was added and the resulting mixture was sat in ice for ~ 3 h to precipitate the KCl. Within 20 minutes of the dahp solution being added to the metal-dfmp solution the reaction mixture had gone bright green and a lot of solid was evident. After ~ 24 h refluxing the reaction mixture was filtered hot through a sintered glass funnel and the bright green powder **48** collected.

Yield : 0·66 g, 0·648 mmol, 64·8 %

IR : 3405, 2915, 1657, 1635, 1550, 1352, 1238, 1228, 878, 823, 787 cm^{-1}

FAB-ms ($^m/_e$) : 908(1), 849(1), 812(2), 794(4), 774(2), 754(3), 736(5), 717(4), 679(37), 643(100), 625(4), 607(23), 550(28), 493(18).

ES-ms ($^m/_e$) : 1373(2), 608(1), 592(3), 493(9), 403(1), 381(8), 305(2), 247(100).

UV : 669·2, 626·0sh, 603·8, 596sh, 417·2

Analysis for : $[Co_2(H_4\mathbf{LV5})Cl_2(H_2O)_2].CoCl_4^{2-}\cdot 4H_2O.CH_3OH$

Calculated :	C : 34·14;	H : 4·94;	N : 5·49 %
Found :	C : 34·15;	H : 4·72;	N : 5·61 %

4 : COBALT WITH THIOCYANATE

LV5 Complexes

(n.b - These products not very soluble so ms very weak.)

Complex 49 : $[Co_2(H_4LV5)Cl_2(NCS)_2]\ 2H_2O$

The dahp solution was made and added to the reaction as previously reported. A suspension of $Co(NCS)_2$ (4 mmol, 0·700 g) in ~ 40 mL of EtOH and a solution of dfmp (2 mmol, 0·382 g) in ~ 40 mL of EtOH were combined and refluxed 120 mins. The refluxing mixture was a blue suspension which became bright green when the dahp was added. The reaction mixture was refluxed 24 h, and filtered hot to collect the product, a forest green powder **49**.

Yield : 0·73 g, 0·958 mmol, 95·8 %

IR : 3401, 2047, 1652, 1539, 1329, 865, 668.

FAB-ms ($^m/_e$) : 919(6), 698(6), 650(6), 546(11), 523(6), 460(100).

UV(CH_3CN) : 624·8,590sh, 420·8, 322·4

UV (DMF) :629, 590sh, 423, 320sh

Analysis for : $[Co_2(H_4\mathbf{LV5})Cl_2(NCS)_3]\cdot 2H_2O$

Calculated :	C : 41·85;	H : 4·31;	N : 11·02 %
Found :	C : 41·99;	H : 4·54;	N : 10·90 %

Complex 50 : $[Co_2(H_4LV5)Cl_2(NCS)_3]\cdot 1\cdot 5H_2O$

The $Co(NCS)_2$ was dissolved in warm EtOH to form a brilliant blue solution. The dfmp dissolved in a mixture of MeOH and EtOH was added and a darker blue solution formed. This mixture was refluxed for 10 mins. When the dahp solution was added the reaction mixture went green. After refluxing 25 h the mixture was filtered hot and the microcrystalline deep forest green product **50** collected in a frit.

Yield : 0·623 g, 0·777 mmol, 77·7 %.

IR : 3401, 2913, 2052, 1653, 1637, 1330, 1226, 864, 668 cm^{-1}

FAB-ms ($^m/_e$) : almost nothing above background.

UV(CH_3CN) : 641·6, 562·4, 401·6sh, 339·2

UV (DMF) : 627, 591sh, 423, 318sh

Analysis for : $[Co_2(H_4\mathbf{LV5})Cl_2(NCS)_3]\cdot 1\cdot 5H_2O$

Calculated :	C : 42·28;	H : 4·23;	N : 11·13 %
Found :	C : 42·24;	H : 4·42;	N : 11·10 %

Complex 51 : $[Co_2(H_4LV5)Cl_2(NCS)_3]\cdot 1\cdot 5CH_3OH$

The $Co(NCS)_2$ was dissolved in 15 mL of dry MeOH and the brilliant blue solution refluxed 10 mins. On addition of dfmp a green-blue solution formed. The dahpCl_2 was dissolved in 10 mL of MeOH, the KOH solution was added, and the mixture sat in ice for 4 h. The solution changed to brilliant deep green on addition of the dahp. After refluxing 44 h the mixture was filtered hot and the microcrystalline deep forest green product **51** collected in a frit. The filtrate was moss green.

Yield : 0·44 g, 0·539 mmol, 53·9 %

IR : 3749, 3377, 2919, 2861, 2062, 1652, 1633, 1543, 1235, 867, 814, 777 cm^{-1}

FAB-ms ($^m/_e$) : almost nothing above matrix.

This product proved to be insoluble in DMSO, DMF, EtOH, MeOH, $CHCl_3$, THF, H_2O, CH_3NO_3, CH_3CN, and various mixtures of these.

Analysis for : $[Co_2(H_4\mathbf{LV5})Cl_2(NCS)_3]\cdot 1\cdot 5CH_3OH$

Calculated :	C : 43·29;	H : 4·47;	N : 10·87 %
Found :	C : 43·18;	H : 4·37;	N : 10·85 %

Complex 52 : $[Co_2(H_4LV5)Cl_2(NCS)_2]\cdot 1\cdot 5H_2O\cdot 2CH_3OH$

After 14 days a very fine forest green powder **52** was recovered from the filtrate of **51**.

Yield : 0·11 g, 0·136 mmol, 13·6 %

IR : 3405, 2912, 2080, 1650, 1630, 1545, 1235, 875, 827, 777 cm^{-1}

This product was only sparingly soluble in almost all solvents tried. FAB-ms tried but restricted by the insolubility.

Analysis for : $[Co_2(H_4\mathbf{LV5})Cl_2(NCS)_2]\cdot 1\cdot 5H_2O\cdot 2CH_3OH$

Calculated :	C : 41·96;	H : 4·80;	N : 10·38 %
Found :	C : 41·99;	H : 4·53;	N : 10·39 %

LV5t Complexes

Complex 53 : $[Co_2(H_4LV5t)Cl_2(NCS)_3]\cdot 1\cdot 5H_2O$

The $Co(NCS)_2$ (2 mmol 0·7 g) was dissolved with warming in 20 mL of dry MeOH to form a deep purple solution. A dftp (2 mmol, 0·408 g) solution was made in dry MeOH and added. The $dahpCl_2$ was dissolved in 20 mL of MeOH, the KOH solution was added, and the mixture sat in ice for 3 h. The reaction mixture changed to a very deep green and some precipitate formed on addition of the dahp. After refluxing 28 h the mixture was left to cool slowly over 2 days. The product was a deep green glassy looking flaky material **53** which had formed around the solvent line of the reaction. This was collected by vacuum filtration.

Yield : 0·24 g, 0·251 mmol, 25·1 %

IR : 3380, 2953, 2061, 1652, ~1630sh, 1538, 1231, 873, 839, 777, 618 cm^{-1}

FAB-ms ($^m/_e$) : 577(20), 460(100).

Analysis for : $[Co_2(H_4\mathbf{LV5t})Cl_2(NCS)_3]\cdot 1\cdot 5H_2O$

Calculated :	C : 46·06;	H : 5·12;	N : 10·16 %
Found :	C : 46·13;	H : 5·10;	N : 10·25 %

Complex 54 : $[Co_2(H_4LV5t)Cl_2(NCS)_3]\cdot 2H_2O$

More solid started appearing in the deep browny-green filtrate of **53** as the filtering was taking place so the volume of this filtrate was reduced and the mixture set aside for slow evaporation. 2 days later a bright green powder **54** was collected.

Yield : 0·53 g, 0·544 mmol, 54·4 %

IR : 3421, 2954, 2065, 1655, ~1630sh, 1536, 1231, 875, 839, 777, 618 cm^{-1}

Analysis for : $[Co_2(H_4\mathbf{LV5t})Cl_2(NCS)_3]\cdot 2H_2O$

Calculated :	C : 44·03;	H : 4·99;	N : 9·71 %
Found :	C : 43·91;	H : 4·91;	N : 9·63 %

5 : COBALT WITH NITRATE

LV5 Complexes

$[Co_3(H_4LV5)Cl(NO_3)_3]\cdot 2H_2O$

$Co(NO_3)_2$ (4 mmol, 1·164 g) and dfmp (2 mmol, 0·324 g) were mixed in ~ 50 mL of dry EtOH and the bright yellow solution refluxed 25 mins. On addition of the dahp, the reaction mixture went dark brown. It was refluxed, without stirring, for 22 h and left to cool to ambient temperature overnight. The product, an orange powder, was collected by vacuum filtration. (dissolved easily in MeOH)

Yield : 0·36 g, 0·415 mmol, 41·5 %

IR : 3431, 3146, 2932, 2430, 1652, 1632, 1543, 1384, 1307, 1232, 1092, 861, 817, 776 cm^{-1}

This IR was one of the first in which features indicative of a binuclear structure were identified. The nitrate peak is not that for a simple anion but much more complicated and would indicate a coordinated, maybe bridging, nitrate.

FAB-ms ($^m/_e$) : 828(20), 766(18), 656(5), 561(28), 525(30), 468(100),

828 : H_2**LV5** + 3Co + 2NO_3 + Cl + H

769 : H_2**LV5** + 2Co + 2NO_3 + Cl + H

Base peak : **Lo-s** + Co

UV (DMF) :659, 596, 414

Analysis for : $[Co_3(H_4$**LV5**$)Cl(NO_3)_3]\cdot 2H_2O$

Calculated :	C : 36·36;	H : 4·14;	N : 10·60 %
Found :	C : 36·48;	H : 4·15;	N : 10·64 %

Although, the analysis looks plausible for the complex speculated it is most likely explained as a combination of binuclear complex and the **Lo-s** - Co complex represented by the base peak in the ms.

Complex 55 : $[Co_2(H_4LV5)Cl_2(NO_3)_2]\cdot H_2O$

$Co(NO_3)_2$ (4 mmol, 1·164 g) and dfmp (2 mmol, 0·324 g) were mixed in ~ 20 mL of dry MeOH and the golden solution refluxed 15 mins. The dahp solution was chilled in ice for 5 h. The combined reaction mixture was a brown colour

and was refluxed for 62·5 h and filtered hot. The product **55** was microcrystalline deep orange brown

Yield : 0·352 g, 0·447 mmol, 44·7 %

IR : 3420, 3127, 2922, 1653, 1632, 1545, 1387, 1358, 861, 817, 775 cm^{-1}

FAB-ms ($^{m}/_{e}$) : 1074(15), 811(25), - very little above background.

Would not dissolve in MeOH, DMSO, DMF, or CH_3CN.

FAB-ms ($^{m}/_{e}$) : solid sample : 792(5), 775·0(5), 763 (7), 727·0(10), 706·0(9), 693(17), 679·0(19), 670(9), 643·0(100), 607·0(66), 578(47), 550·1(49), 520·9(21).

UV (DMF) :653, 598, 414

Analysis for : $[Co_2(H_4\mathbf{LV5})Cl_2(NO_3)_2]\cdot H_2O$

Calculated :	C : 40·84;	H : 4·65;	N : 10·24 %
Found :	C : 40·85;	H : 4·61;	N : 10·23 %

6 : TOWARD SYNTHESIS OF A HETERO-TETRANULEAR COMPLEX

Two different syntheses have been tried.

Complex **46** (0·0377 g, 4·32 x 10^{-5} m) was dissolved in DMF to form a golden brown solution. Two equivalents of $Cu(NO_3)_2\cdot 3H_2O$ (0·012 g, 8·46 x 10^{-5} m) disolved in MeOH was added to the stirring solution and the expected colour change to bright green was observed. Six equivalents of $AgNO_3$ dissolved in MeOH with a few drops of DMF was added dropwise and the mixture stirred for 4 hours. A white precipitate was filtered off and the resulting solution set aside for crystallisation; by slow evaporation and ether diffusion.

In the second preparation the same quantities were used but the silver salt was added to the cobalt solution and the mixture stirred and filtered through a pipette stuffed with glass wool. This process was repeated until the resulting solution was clear and on the final filtration was dripped into a stirring solution of $Cu(NO_3)_2$. The resulting green-brown solution was also set up for crystallisation.

Crystal data and structure refinement for Complex 31

Empirical formula	$C_{32}H_{38}Cl_4Co_2N_4O_{14}$
Formula weight	1080.18
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 9.308(3) Å alpha = 86.410(10)
	b = 10.803(2) Å beta = 76.38(2)
	c = 10.826(3) Å gamma = 74.16(3)
Volume, Z	1017.8(5) $Å^3$, 1
Absorption coefficient	1.828 mm^{-1}
F(000)	546
Crystal colour and form	Golden block
Crystal size	0.64 x 0.12 x 0.1 mm
Theta range for data collection	2.29 to 22.49 deg.
Limiting indices	0<h<9, -11<k<11, -12<l<12
Reflections collected	3014
Independent reflections	2793 [R(int) = 0.0373]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2793 / 12 / 370
Goodness-of-fit on F^2	1.095
Final R indices [I>2sigma(I)]	R1 = 0.0895, wR2 = 0.2239
R indices (all data)	R1 = 0.1237, wR2 = 0.2511
Largest diff. peak and hole	1.231 and -.723 $e.A^{-3}$

Crystal data and structure refinement for Complex 32

Empirical formula	$C_{32}H_{38}Cl_4Co_4N_4O_{14}$
Formula weight	1080.18
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 8.711(4) Å alpha = 102.99(6)°
	b = 10.931(8) Å beta = 95.97(6)°
	c = 11.902(10) Å gamma =99.71(4)°
Volume, Z	1076.5(13) $Å^3$, 1
Density (calculated)	1.666 Mg m^{-3}
Absorption coefficient	828 mm^{-1}
F(000)	546
Crystal colour and form	Golden block
Crystal size	0.69 x 0.35? x 0.28 mm
Theta range for data collection	2.29 to 22.49 deg.
Limiting indices	0<h<9, -11<k<11, -12<l<12
Reflections collected	3014
Independent reflections	2793 [R(int) = 0.0373]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2793 / 12 / 370
Goodness-of-fit on F^2	1.095
Final R indices [I>2sigma(I)]	R1 = 0.0895, wR2 = 0.2239
R indices (all data)	R1 = 0.1237, wR2 = 0.2511
Largest diff. peak and hole	1.231 and -.723 e.A^{-3}

Crystal data and structure refinement for Complex 33

Empirical formula	$C_{30}H_{38}Cl_4Co_2N_4O_{14}$
Formula weight	1160.09
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 8.711(4) Å α = 102.99(6) deg.
	b = 10.931(8) Å β= 95.97(6) deg.
	c = 11.902(10) Å γ = 99.71(4) deg.
Volume, Z	1076.5(13) $Å^3$, 1
Density (calculated)	1.789 Mg/m^3
Absorption coefficient	2.757 mm^{-1}
F(000)	581
Crystal colour and form	Golden block
Crystal size	0.46 x 0.36 x 0.36 mm
Theta range for data collection	2.29 to 27.61 deg.
Limiting indices	0<h<11, -13<k<13, -15<l<15
Reflections collected	5227
Independent reflections	4903 [R(int) = 0.0211]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4903 / 0 / 284
Goodness-of-fit on F^2	1.827
Final R indices [I>2sigma(I)]	R1 = 0.1192, wR2 = 0.2979
R indices (all data)	R1 = 0.1704, wR2 = 0.3172
Largest diff. peak and hole	1.785 and -1.463 $e.Å^{-3}$

Crystal data and structure refinement for Complex 40

Empirical formula	C34H60Cl4Co2N4O10
Formula weight	944.52
Temperature	130(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.2900(10) A α= 63.440(10)°
	b = 11.078(2) A β = 84.980(10)°
	c = 11.365(2) A γ = 65.850(10)°
Volume, Z	1050.1(3) A^3, 1
Density (calculated)	1.494 Mg/m^3
Absorption coefficient	1.101 mm^{-1}
F(000)	494
Crystal form and colour	Golden bock
Crystal size	52 x .22 x .16 mm
Theta range for data collection	2.02 to 27.50 deg.
Limiting indices	0<=h<=13, -11<=k<=12, -14<=l<=14
Reflections collected	4900
Independent reflections	4613 [R(int) = 0.0177]
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	1.00 and .913
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4613 / 0 / 364
Goodness-of-fit on F^2	0.976
Final R indices [I>2sigma(I)]	R1 = 0.0319, wR2 = 0.0748
R indices (all data)	R1 = 0.0451, wR2 = 0.0776
Largest diff. peak and hole	.807 and -.341 $e.A^{-3}$

Crystal data and structure refinement for Complex 44

Empirical formula	C26.67 H45 Cl4 Co2 N5.33 O6.33
Formula weight	801.34
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 13.373(3) Å alpha = 90°.
	b = 17.321(4) Å β= 100.010(10)°
	c = 26.438(5) Å γ = 90°.
Volume, Z	6031(2) A^3, 6
Density (calculated)	1.324 Mg/m^3
Absorption coefficient	1.132 mm^{-1}
F(000)	2490
Crystal form and colour	Bright green block
Crystal size	1.10 x 0.9 x 0.36 mm
Theta range for data collection	2.19 to 24.99 deg.
Limiting indices	0<h<15, 0<k<20, -31<l<30
Reflections collected	5529
Independent reflections	5283 [R(int) = 0.0495]
Absorption correction	Psi-scans
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5262 / 0 / 297
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0772, wR2 = 0.2298
R indices (all data)	R1 = 0.1114, wR2 = 0.2824
Largest diff. peak and hole	1.578 and -0.905 $e.A^{-3}$

CHAPTER 6

THE MANGANESE COMPLEXES

1 : INTRODUCTION

The most common oxidation state shown by manganese is the +2. As Mn(II) is a d^5 (usually high spin) ion it is not affected by crystal-field stabilisation energies and consequently it exhibits a large variety of complexes and stereochemistries. Octahedral and tetrahedral geometries are common for Mn(II). In contrast the complexes of Mn(III) exhibit regular angles around the ion but because of Jahn-Teller distortion the geometry is likely to be tetragonal. The geometric preferences which contribute to the different oxidation states of manganese in bioinorganic chemistry are not yet well understood. It does seem probable that in biological systems geometry is exploited, either where the manganese does not have a redox function to restrict access to potentially hazardous higher oxidation states, or to allow oxidation states higher than +2 where a redox function is involved.

Nelson and M^{c}Kee[227] have investigated the circumstances under which a particular donor set will stabilise the II, III and IV states of Mn. A cryptand, containing three phenolate-O^- and three imino-N donor sets, which had been specifically designed for the complexation of +3 oxidation states of Group 13 and lanthanides,[224,228] was reacted with Fe(II), Fe(III), Mn(II) and (Mn(III) salts. It was found that while the mono-Fe(III) product was formed only mono-Mn(II) products were isolated. Crystal structures of an Fe(III) and two Mn(II) complexes showed distortion of the octahedral geometry towards a trigonal prismatic arrangement and while this is acceptable to the d^5 cations Fe^{III} and Mn^{II} the reduced Fe^{II} (d^6) and the oxidised Mn^{III} (d^4) states have more specific geometric requirements which cannot easily be met within the rigid cryptand framework. However it is noted that where ligands with exactly the same donor set, but lacking the built in rigidity of the cryptand, are used square based octahedral or tetragonal sites are achievable. Template synthesis of two

examples of such ligands on Mn(II) generated Mn^{3+} [229] and Mn^{4+} [230] complexes respectively. In both these structures the angles at the Mn ion are close to 90°. The Mn^{III} complex exhibits the expected Jahn-Teller tetragonal distortion but the Mn^{IV} complex for which such a distortion is not required, has a regular, almost octahedral, structure. The authors conclude that given the identical donor set across this series of ligands, the redox preference is due to geometric factors.

It would be expected that like the cobalt complexes, manganese complexes of **LV5** and **LV5t** would not be planar in the presence of acetate donors. The flexibility of this ligand system should be able to accommodate a range of mixed valence complexes. Formation of both binuclear and tetranuclear complexes was likely. McKee *et. al.* had synthesised[47] a mixed valence tetranuclear $Mn^{II}_2Mn^{III}_2$ macrocyclic complex (refer Section 2) of the **LV5** ligand system and it was hoped that the remaining complexes (*) in the tetranuclear series might be filled.

*	$Mn_2^{II}Mn_2^{III}$	*	*

The manganese complexes synthesised in this project were isolated as powders and although some crystals were obtained none of them was good enough for X-ray crystal structure analyses. In the absence of any crystal structures the manganese complexes were identified by mass spectral, infra-red and analysis data. The reaction products often appear to be a complex mixture of polymeric materials (in small amounts) and macrocyclic complexes.

2 : THE ACETATE COMPLEXES

The tetranuclear macrocyclic complex of the **LV5** ligand system already reported by McKee[47] was mixed valence $Mn^{II}_2Mn^{III}_2$. This complex was made using manganese acetate as the templating salt and the brown crystals used for the X-ray study were obtained from recrystallisation from a mixture of methanol and ether. Figure 6·1 shows the macrocyclic core of the $[Mn^{II}_2Mn^{III}_2(\mu_4\text{-}O)$**LV5**$(CH_3COO)_3Cl(CH_3OH)]\cdot 3CH_3OH$ complex. In contrast to the tetracopper complexes of **LV5** the manganese macrocycle is not planar.

The mean planes of the two phenol rings are inclined at an angle of 38·5 ° to each other. All the alcohol and phenol groups are deprotonated and each bridges two manganese ions. The complex core also contains a μ_4-O group, three bridging acetate groups, a chloride ion and a methanol molecule. Three uncoordinated methanol molecules are found in the asymmetric unit.

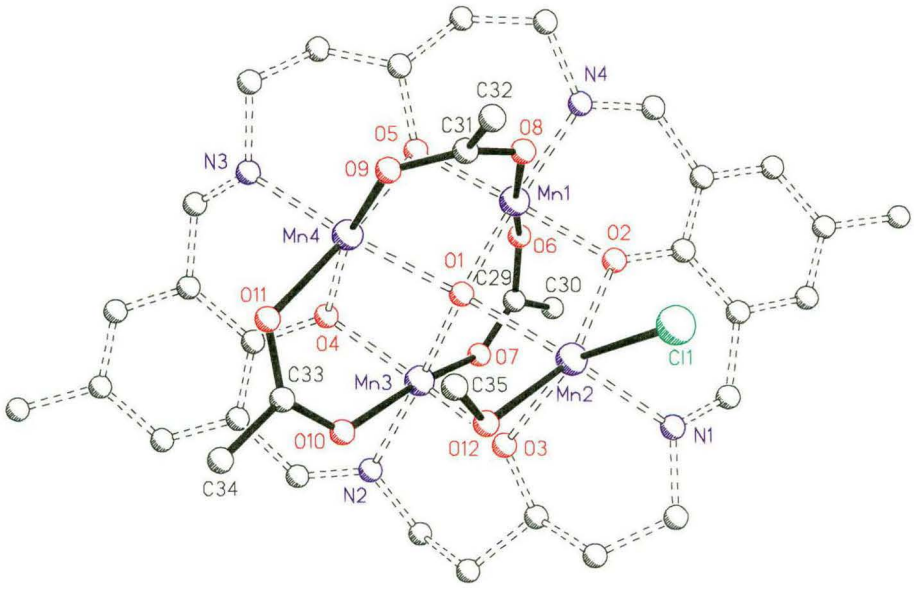


Figure 6·1 : The $[Mn^{II}_2Mn^{III}_2(\mu_4\text{-O})LV5(CH_3COO)_3Cl(CH_3OH)]\cdot 3CH_3OH$ core of complex M19

Figure 6·2 shows detail of the coordination spheres of the metal ions. Mn1 and Mn3 are both six-coordinate and have approximately octahedral geometry; being coordinated to the macrocycle via one imine nitrogen, one phenoxy oxygen and one alkoxy oxygen. Each is also bound to two acetate groups (*trans* to each other) and to the central oxo ion. Mn2 and Mn4, while also being six coordinate, have much less regular geometry than the other metal ions. The donor set for Mn4 is the same as for Mn1 and Mn3 but the acetate groups are in a *cis* arrangement. The coordination sphere of Mn2 is completed by a chloride ion and a methanol molecule. Mn1 and Mn3 are assigned +3 oxidation levels whereas Mn2 and Mn4 are assigned +2. This was decided on the basis of the overall stoichiometry of the complex and an examination of the bond lengths around the metal ions. The bond distances around Mn1 and Mn3 are very similar and significantly shorter than the equivalent bonds for Mn2 and Mn4. Similar distinctions in bond lengths have been made in other $Mn^{II}Mn^{III}$

mixed-valence systems[159, 231] and in the mixed valence cobalt structures discussed in Chapter 4.

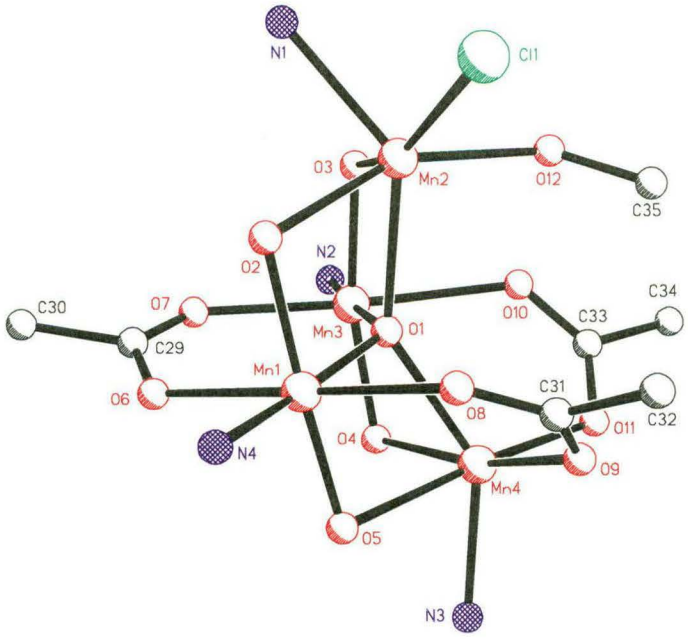


Figure 6·2 : The coordination spheres of the manganese ions in M19

2·1 : Acetate Complexes with LV5

Table 6·1 : Acetate Complexes with LV5

56	$[Mn_4(\mu_4\text{-}O)\mathbf{LV5}Cl(CH_3COO)_4]\cdot CH_3OH\cdot 5H_2O$
57	$[Mn_4\mathbf{LV5}(CH_3COO)_4Cl_3]$ & $[Mn(H_2\mathbf{Lo\text{-}s})(CH_3COO)]\cdot 2CH_3CH_2OH$
58	$[Mn_2(H_3\mathbf{Lo\text{-}s})Cl_2]\cdot MnCl_4^{2-}\cdot CH_3OH\cdot 2H_2O$
59	$[Mn_4\mathbf{LV5}Cl_2(CH_3COO)_3(CH_3COOH)]\cdot MnCl_4^{2-}\cdot 2CH_3CH_2OH\cdot CH_3OH\cdot 2H_2O$
60	$[Mn_4\mathbf{LV5}Cl_3(CH_3COO)_4]\cdot CH_3CH_2OH\cdot 3H_2O$
61	$[Mn_2(H_2\mathbf{Lo\text{-}s})(2\cdot 5Cl)(CH_3COO)(0\cdot 5OH)]$
62	$[Mn_4\mathbf{LV5}(CH_3COO)_2(CH_3COOH)_2Cl_4][Mn_2Cl_4\cdot 3H_2O]\cdot 2H_2O$
63	$[Mn_4\mathbf{LV5t}(dftp)_2Cl_2(OH)_2]\cdot CH_3OH$

Table 6·2 : Selected IR frequencies (cm^{-1}) of acetate complexes of LV5

56	3418		1645	1630		1566		1414		968	891	822		768	
57	3474	1661		1623	1599	1547	1453	1394		960	891			763	744
58	3410	1665		1624	1600	1549	1452	1396		958	881			763	745
59	3421		1646			1570	1451	1411		961	890	822		770	
60	3415			1625		1558	1447	1405		963	892	823		766	
61	3403			1629		1554	1448	1418		975		829	812	773	
62	3422	1667		1624	1603					959		834		764	745
63	3426			1627		1549	1450	1418	1384	983		842	816		737

Manganese acetate and dfmp were refluxed together in boiling EtOH for 10 minutes before the addition of the dahp solution. After a 24 h reflux period the

reaction mixture was allowed to cool, with stirring, for 3 days after which time as no product was visible, the now almost black solution was transferred to a beaker and allowed to evaporate slowly. After 10 days the mixture, which had reduced to a black oil, was redissolved in MeOH and aliquots set up for ether diffusion. Eventually an unidentified black powder, some black crystals (complex **56**) and a dark brown powder (complex **57**) were retrieved from these. The residue of these products was redissolved in MeOH and ether diffused into this solution. Complex **58** was isolated from this. Complex **56** is identified as being tetranuclear by a fingerprint pattern, similar to that identified in the cobalt complexes, in the IR spectrum (Table 6·2) and FAB-ms ions (Table 6·3). The chemical analysis closely matches $[Mn_4(\mu_4\text{-}O)\mathbf{LV5}Cl(CH_3COO)_4]\cdot CH_3OH\cdot 5H_2O$ which suggests that the complex contains one Mn(II) ion and three Mn(III) ions and thus fills one of the places in the hoped for series. Alternate formulations containing one or more bound acetic acid groups are equally valid. No carbonyl peak (as expected for an acetic acid group) is seen in the IR of this complex and this could be taken as supporting a $Mn^{II}Mn^{III}_3$ complex. The FAB-ms of **57** suggests that it is a mixture of a tetranuclear and an open-sided complex and features for both are seen in the IR (Table 6·1). The analysis fits a 50 : 50 mix of both $[Mn_4\mathbf{LV5}(CH_3COO)_4Cl_3]$ and $[Mn_2(H_2\mathbf{Lo\text{-}s})(CH_3COO)]\cdot 2CH_3CH_2OH$. The third product of this reaction (**58**) is an open-sided complex and is formulated as $[Mn_2(H_3\mathbf{Lo\text{-}s})Cl_2]\cdot MnCl_4^{2-}\cdot CH_3OH\cdot 2H_2O$. The charge balance of this complex and the microanalysis are satisfied by the inclusion of the $MnCl_4^{2-}$ anion.

It is well known that many and varied, both charged and neutral, manganese chloride compounds exist. Chemical analysis results indicate that many of the products from the Mn - **LV5** syntheses, while being homogenous, are not pure macrocyclic complexes. It is suggested that these contain, at least small amounts, of examples of these Mn-Cl moieties and this is supported by polymeric repeating patterns in the lower mass range of the FAB-ms spectra of many products. L'Haridon reported the crystal structure of the neutral species $Mn_2Cl_4\cdot 3CH_3CH_2OH$ (Fig. 6·3). It is suggested variations of this moiety involving ethanol, methanol or water molecules, e.g. $[Mn_2Cl_4\cdot 3H_2O]$ in complex **62**, are present some products.

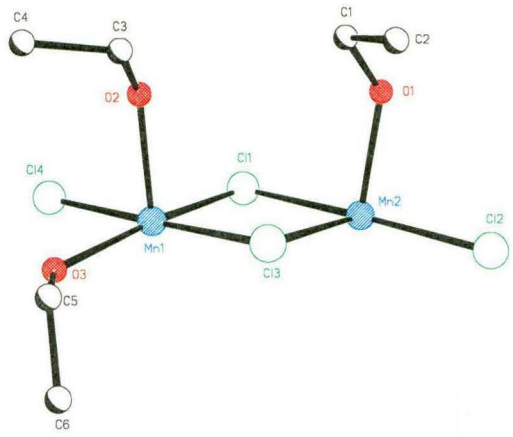


Figure 6·3 : $Mn_2Cl_4{\cdot}3CH_3CH_2OH$

Table 6·3 : Selected FAB-ms ions for LV5 - OAc complexes

LV5 + OAc		56	57	58	59	60	61	62
LV5, 4Mn, 4OAc, 3Cl,	1049·0		1051·2		1047·0			1051·1
LV5, 4Mn, O, 4OAc, Cl	995·1	995·0						
LV5, 4Mn, O, 4OAc, OH	977·1					977·6		
LV5, 4Mn, O, 4OAc	960·0	960·0						
LV5, 4Mn, 3OAc, 2Cl	954·9				953·9			
LV5, 4Mn, O, 3OAc, Cl	936·0	936·0						
LV5, 2Mn, 5OAc, Cl	928·2				929·8			
LV5, 4Mn, O, 3OAc, O	917·0	915·0						
LV5, 4Mn, O, 3OAc	901·0	901·0			900·8			901·1
LV5, 4Mn, 3OAc	885·0	885·0	887·1					
LV5, 4Mn, OAc, 3Cl	873·7				875·8			875·9
LV5, 4Mn, 2OAc, Cl	861·9		860·1				865	
LV5, 2Mn, OH, 4OAc	851·2						850·4	
LV5, 4Mn, O, 2OAc	842·0	842·0			841·8	841·9		842·1
LV5, 2Mn, OH, 3OAc, Cl	827·1					827·9		
LV5, 4Mn, O, OAc, Cl	818·8		820·1		817·8	817·9		818·0
LV5, 4Mn, OAc, Cl	802·0		804·0		800·8			
LV5, 4Mn, O, OAc,	783·0				782·8	782·8	783·3	782·9
LV5, 4Mn, 2Cl	777·9		777·0					
LV5, 2Mn, OH, 2OAc, Cl	768·1					768·2		766·9
LV5, 4Mn, O, Cl	758·9				758·8	758·8		759
H_2**Lo-s**, 2Mn, 2OAc, 3Cl	741·9				740·8	740·9	743·4	
LV5, 2Mn, O, 3Cl	719·0				719		719·3	
H_2**Lo-s**, 2Mn, OAc, 4Cl	699·9						699·3	
H_2**Lo-s**, 2Mn, OAc, 3Cl, OH	682·9						683·4	682·0
LV5, 2Mn, OAc, O	673·1			673·2				
H_2**LV5**, 2Mn, OAc,	659·1							659·1
H_2**Lo-s**, 2Mn, 2OAc	637·1			633		637		635·1
H_2**LV5**, 2Mn, H**Lo-s**, Mn, 2OAc, OH	600·1					599·0	599·2	599·1
Lo-s, 2Mn, 2Cl	587·9		588·0					
H_2**Lo-s**, 2Mn, OH, Cl	571·0						570·2	
H_4**Lo-s**, 2Mn, OH	538·0							539·2
Lo-s, 2Mn,	517·0		517·0				514·2	516·9
Lo-s, Mn, Cl	497·1			497·1				497
LV5	488·2					487·9		
Lo-s, Mn, OH	479·1			480·0				
H_2**Lo-s**, Mn,	464·1		464·1	464·0		464·0		464

When the same reaction was repeated with a 48 h refluxing time and allowed to evaporate slowly over 12 days, a few tiny dark brown crystals formed. The IR of these indicated that a tetranuclear product had formed but they were not good enough for X-ray analysis and there was not enough for other investigations to be made. The filtrate from which the crystals had been separated was warmed and ether added. After considerable time a dark brown flaky material (complex **59**) was collected from this. The IR of this product shows some distinct differences, in the imine area, to those usually seen in the IRs of these macrocyclic complexes. A pattern indicative of a tetranuclear product (Table 6·2) is seen in the carbon skeleton area of the spectrum. Only ions for tetranuclear products (Table 6·3) are seen in the FAB-ms. From this and the analysis **59** has been assigned the formula $[Mn_4\mathbf{LV5}Cl_2(CH_3COO)_3(CH_3COOH)]\cdot MnCl_4^{2-}\cdot 2CH_3CH_2OH\cdot CH_3OH\cdot 2H_2O$.

Some of **59** was dissolved in CH_2Cl_2 and eventually a very fine pale brown powder (complex **60**) collected. $[Mn_4\mathbf{LV5}Cl_3(CH_3COO)_4]\cdot CH_3CH_2OH\cdot 3H_2O$ gives a good fit for the analysis of complex **60** suggesting a $Mn^{II}Mn^{III}_3$ complex. Peaks for ions of an open-sided complex are seen in the FAB-ms of complex **60** and this points up another dilemma when designating formulae to lots of the products synthesised in this project. The possibility that the open-sided complex is a break down product within the mass spectrometer has always been considered and where complexes are designated to be open-sided it is because a peak at ~1660 cm^{-1} in the IR indicates the open-side. Of course for any complexes made using the acetate ion an alternate explanation for this peak is the presence of acetic acid rather than acetate groups. The pale colour of **60** was thought to be because of the fineness of the powder but if **60** contains acetic acid groups in place of some of the acetate groups then more of the manganese ions would be Mn^{II} and the colour could be pale.

A reaction carried out in the presence of TEA yielded a tiny amount of dark brown powder, complex **61**, from the cooled mixture. IR and FAB-ms identify this as an open-sided complex and from analysis it is assigned the formula $[Mn_2H_2\mathbf{Lo\text{-}s}(2{\cdot}5Cl)(CH_3COO)(0{\cdot}5OH)]$. The remaining reaction mixture was evaporated to dryness and EtOH added. The resulting dark brown micro-

crystalline product, (complex **62**) formulated as $[Mn_4$**LV5**$(CH_3COO)_2(CH_3COOH)_2Cl_4]\cdot[Mn_2Cl_4\cdot 3H_2O]\cdot 2H_2O$ was collected by vacuum filtration. An alternative possibility for the formula of complex **62** is Mn_4**LV5** $(CH_3COO^-)_2(CH_3COOH)_2Cl_4]\cdot Mn_2Cl_4^{2-}\cdot 4H_2O$ which would mean that the complex is Mn^{III}_4 and its very dark brown colour could be indicative of this. Although the FAB-ms is dominated by peaks for a tetranuclear complex, ions for an open-sided complex are also seen.

2·2 : The acetate complex with LV5t

Only one product was identified from the reactions carried out with **LV5t** and manganese acetate. The reactions were carried out with and without the addition of TEA and/or NH_4NCS. Ions in the FAB-ms indicate that most of the products are complicated mixtures of polymeric products and tetranuclear complexes. No ions for open-sided complexes are seen in any of these spectra. Analytical data for **63** closely match a formula similar to the folded macrocyclic ligand reported in the copper section and is assigned $[Mn_4$**LV5t**$(dftp)_2Cl_2(OH)_2]\cdot CH_3OH$. IR and FAB-ms data are shown in tables 6·1 and 6·4.

Table 6·4 : FAB-ms for 63

LV5t + OAc		**63**
LV5t , 4Mn, 4OAc, OH	1045·1	1045·8
LV5t , 4Mn, 4OAc	1028·1	1028·1
LV5t , 4Mn, O, 2OAc	926·1	926·1
LV5t , 4Mn, O, OAc	867·1	867·0
LV5t , 4Mn, O, Cl	843·0	843·0

3 : THE PERCHLORATE COMPLEXES

Table 6·5 : Perchlorate complexes of LV5 and LV5t

64	$[Mn_2(H_4$**LV5**$)Cl_3(ClO_4)]\cdot 2H_2O\cdot CH_3CH_2OH$
65	$[Mn_2(H_4$**LV5**$)Cl_2(ClO_4)(CH_3CH_2O)]$
66	$[Mn_2(H_4$**LV5**$)(ClO_4)Cl_3]\cdot 2H_2O\cdot CH_3OH$
67	$[Mn_2(H_4$**LV5**$)(ClO_4)_2(OH)_2]\cdot CH_3CH_2OH$
68	$[Mn_2(H_4$**LV5**$)(ClO_4)_3Cl_2]\cdot 2{\cdot}5CH_3CH_2OH$
69	$[Mn_2(H_4$**LV5t**$)(ClO_4)_4Cl]\cdot CH_3CH_2OH\cdot 3H_2O$

The seven complexes identified from reactions between **LV5** and **LV5t** and manganese perchlorate (Table 6·5) are all identified as being binuclear complexes of either the full or open-sided ligands. There were similarities to the binuclear pattern observed in the cobalt structures, in some of the IR spectra (Table 6·6), but on the whole none of these was definitive. No peaks for ions of tetranuclear fragments were found in any of the FAB-ms spectra of these complexes (Table 6·7) and the analyses support the formation of binuclear complexes. It is speculated that these complexes are similar to the binuclear cobalt complexes discussed in Chapter 5 and to the binuclear manganese complex of the related **AmP** ligand reported by Robson.[165] From the structure of these complexes it would be expected that the manganese ions would be in positions diagonally opposed to each other within the macrocyclic framework and that they would be bridged by one or more anions as shown in Figure 6·4. The proton shift from the phenolic oxygen to the imine, which has been oserved in all the reported stuctures, would also be expected to have occurred. The flexibility of the **LV5** allows the regular geometry around manganese ions in the +3 or even the +4 oxidation oxidation states. Octahedral geometry was oserved at the cobalt ions in the cobalt binuclear complexes.

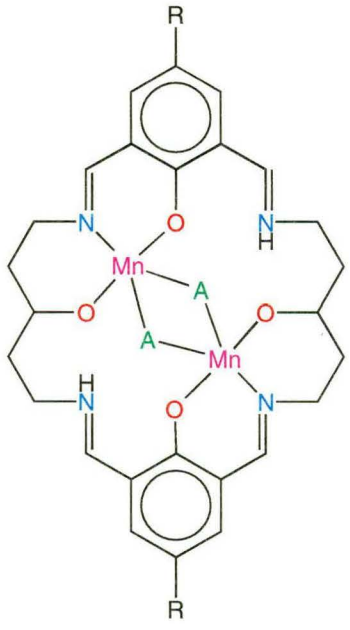


Figure 6·4 : Proposed structure of the Binuclear Manganese Complexes
A = Bridging anionic species.

The binuclear manganese complex reported by Robson was formed by template condensation on $Mn(CH_3COO)_2$ in boiling MeOH and crystals were

isolated after the saturating the cooled reaction mixture with dioxygen. Although Ni_4 and Zn_4 complexes of this ligand system have been characterised no tetranuclear manganese complexes were isolated. Figure 6·5 shows the cationic core of complex **M20** $[Mn_2(H_2\textbf{LAmP})(\mu_2\text{-}OOCCH_3)(\mu_2\text{-}OH)(CH_3OH)_2]\cdot 2ClO_4\cdot 2H_2O$. Each manganese ion is in a six-coordinate, Jahn-Teller tetragonally distorted environment as expected for Mn^{3+} with a high-spin d^4 configuration. Angles at the manganese ions range from 81·3(3)° to 96·8(3)°. The coordination plane (defined by O1, O2, N1 and O4) around Mn1 is inclined at a dihedral angle of 58·5° to the analogous plane around Mn1a

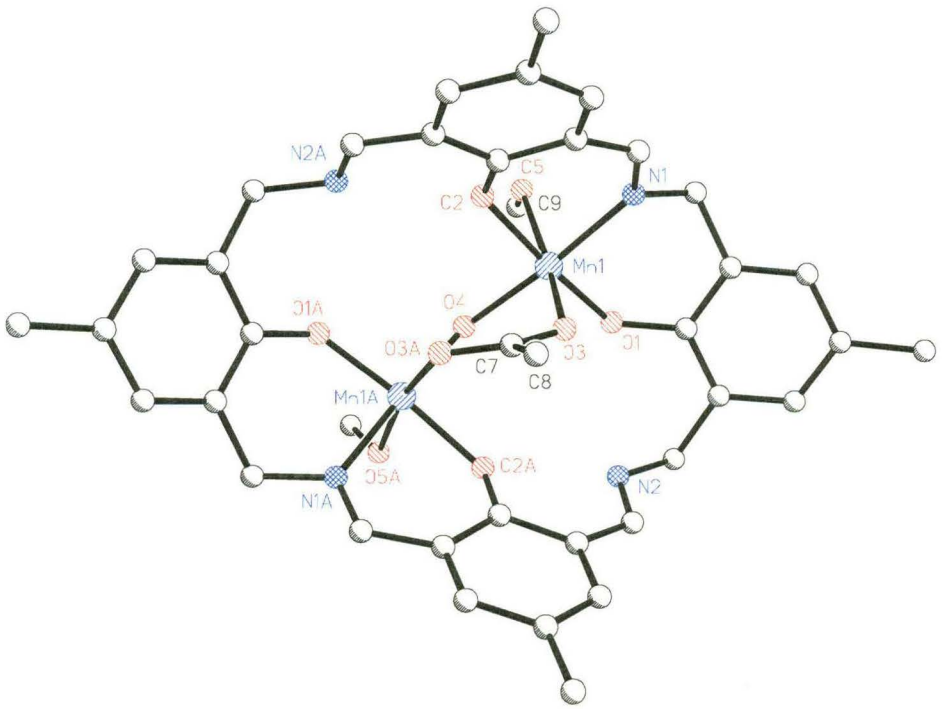


Figure 6·5 : The $[Mn_2(H_2LAmP)(\mu_2\text{-}OOCCH_3)(\mu_2\text{-}OH)(CH_3OH)_2]^{2+}$ core of M20

As for previously reported complexes of this ligand system the manganese complex has a bowl-like conformation with all four phenol rings inclined on the same side of a plane defined by the four nitrogen atoms. A proton shift has occurred from dialdehyde derived phenols to the imine nitrogens and protons are found on the diamine derived phenols. This is similar to the binuclear cobalt complexes of **LV5** reported in Chapter 5 where the alcohol oxygens of the lateral chains remain protonated and a proton shift from the dialdehyde phenols to the imine nitrogens is observed.

Table 6·6 : Selected IR frequencies (cm-1) for LV5 and LV5t - ClO_4 complexes

64	3439		2925	1661		1638	1532	1108		625
65	3424		2925		1653		1534		1098	625
66	3427	3230	2924	1663		1637	1533		1096	624
67	3407		2923	1663		1640	1529	1128	1079	625
68	3435	3223	2924	1667		1627	1560		1088	625
69	3364	3236	2953		1659	1624	1556		1082	621

Complexes **64**, **65**, and **66** are the sequential products from a reaction in which manganese perchlorate and dfmp were refluxed in dry EtOH before the addition of dahp. The reaction mixture was refluxed for 24 h before cooling slowly with stirring. The initial product, a yellowish-brown powder, which appears to be a mixture of a binuclear complex and a manganese salts, was collected by vacuum filtration from the dark brown mixture; apparently an homogenous mixture of a macrocyclic complex and a manganese salt. The second product, another yellow-brown powder, **64** $[Mn_2(H_4\mathbf{LV5})Cl_3(ClO_4)] \cdot 2H_2O \cdot CH_3CH_2OH$ formed in the filtrate overnight. The filtrate was reduced under vacuum and set up for ether diffusion. After 7 days the solid which had precipitated was stirred in dry MeOH, and undissolved yellow-brown cake **65** $[Mn_2(H_4\mathbf{LV5})Cl_2(ClO_4)(CH_3CH_2O)]$ collected. The remaining filtrate was again set up for ether diffusion and an orangey-brown powder eventually collected. Samples of this were dissolved in N,N-dimethylacetamide, dmf, and ethyl acetate. Some microcrystalline material **66** $[Mn_2(H_4\mathbf{LV5})(ClO_4)Cl_3] \cdot 2H_2O \cdot CH_3OH$ was collected from the ethyl acetate portions. Features in the IR (Table 6·6) indicate that products **64** (1661 cm^{-1}) and **66** (1663 cm^{-1}) contain at least traces of an open-sided complexes.

Table 6·7 : Selected FAB-ms ion for LV5 - ClO_4 complexes

LV5 + ClO_4		**64**	**65**	**66**	**67**	**68**
H_3**Lo-s**, Mn, $3ClO_4$	763·8		763·3			
H_2**LV5**, 2Mn, Cl, ClO_4	735·1			735		735
H_2**LV5**, 2Mn, ClO_4	699·1	699·1	699·2	699·1	699	698
H_2**LV5**, 2Mn, 2Cl	671·4			671·1		
H**Lo-s** , Mn, $2ClO_4$	662·3	662·1				
H_2**LV5**, 2Mn, Cl,	635·1					
H**LV5**, Mn, H_2O	599·1		599·2		599	598
H_2**Lo-s**, Mn, Cl, ClO_4,						
H_3**LV5**, Mn, H_2O	564·2		564·2		564	564
H_2**Lo-s**, Mn, ClO_4, H	563·9					
H_4**LV5**, Mn	546·2					
H_4**LV5**, H	493·6		493·3		493	
H_2**Lo-s**, Mn	464·1	464·1	464·2		464	464

Manganese perchlorate was used in one of a series of reactions in which only two metal equivalents were used. After refluxing for 23 h the dark brown reaction mixture was cooled to room temperature and a very fine tan coloured powder (Complex **67**) separated 2 days later. The filtrate was allowed to evaporate slowly and after considerable time yielded a khaki powder (Complex **68**) and a few black crystals which were not suitable for X-ray analysis. Ions for both full and open-sided complexes can be seen in the FAB-ms of both **67** and **68**. Although the analysis of each of these products can be made to closely fit a binuclear complex of the full macrocycle the IRs (Table 6·6) of both show peaks (**67** -1663 cm^{-1} and **68** -1667 cm^{-1}) indicative of open-sided complexes being present. Clearly (from the analysis and the ms) both of these are present. The separation of these products and their clean up is clearly the next challenge in this project and to this end column chromatographic techniques are to be investigated. It is thought that the presence of more than one complex is one of the reasons that crystallisation attempts have not been successful.

The $Mn(ClO_4)_2$ - **LV5t** reaction mixture was refluxed for 25h after which time a significant amount of a pale yellow solid separated. This was shown by IR to be predominantly inorganic. The dark brown filtrate evaporated to dryness and MeOH added. The undissolved material (Complex **69**) was a dark moss-green solid. Complex **69** is assigned the formula $[Mn_2(H_4\textbf{LV5t})(ClO_4)_4Cl]\cdot CH_3CH_2OH\cdot 3H_2O$ based on the IR (Table 6·6), the analysis, and FAB-ms (Table 6·8). The green colour of **69** is indicative of the presence of Mn^{III} and the above formula is for a mixed valence $Mn^{II}Mn^{III}$ complex.

Table 6·8 : Selected FAB-ms ions for 69

LV5t + ClO_4		**69**
H_2**LV5t** , 2Mn, Cl, ClO_4	819·2	819·3
H_2**LV5t** , 2Mn, ClO_4	783·2	783·3
H_2**LV5t** , 2Mn, 2Cl, H	755·2	755·3
H_3**LV5t** , Mn, ClO_4, H	730·3	730·4

No complexes have been unequivocally identified from the products of the reactions in which TEA was added to the reaction mixtures when either the **LV5** or the **LV5t** ligand system was involved.

4 : THE CHLORIDE COMPLEXES

Table 6·9 : Chloride complexes of LV5 and LV5t

70	$[Mn_4(\mu_4\text{-}O)\mathbf{LV5}Cl_5]\cdot H_2O\cdot CH_3OH$
71	$[Mn_4\mathbf{LV5}Cl_2]\cdot MnCl_4^{2-}\cdot 2H_2O$
72	$[Mn_4\mathbf{LV5t}Cl_5]\cdot MnCl_4^{2-}\cdot 3H_2O\cdot CH_3OH$
73	$[Mn_4\mathbf{LV5t}Cl_6]\cdot 2Mn_2Cl_4\cdot 4H_2O\cdot 2CH_3OH$

A number of products in very good yields were isolated from the **LV5** and **LV5t** reactions with $MnCl_2$. They were either green, green-brown or orange powders. All four of the complexes assigned formulae (Table 6·9) are tetranuclear.

Table 6·10 : Chloride complexes of LV5 and LV5t and selected IR frequencies (cm-1)

70	3320		2905		1637	1551	970	898-877	843	811	772	
71	3308		2919	1652		1538		865		812	779	
72	3404		2956	1650	1626			895	842		780	765
73	3372	3217	2957	1657	1627				842		778	757

The reaction mixture from which complex **70** was collected included TEA. The product, a very fine greeny-brown powder, was filtered from the dark brown mixture after 22h of refluxing. The FAB-ms of this product is dominated by peaks for ions of a tetranuclear complex. From the analysis the proposed formula is $[Mn_4(\mu_4\text{-}O)\mathbf{LV5}Cl_5]\cdot H_2O\cdot CH_3OH$ which is a mixed valence $Mn^{II}Mn^{III}_3$ complex; this is supported by the green colour. When the reaction was carried out without the presence of TEA an orange solid formed almost immediately the dahp solution was added to the refluxing metal salt and dfmp. Again the reflux time was 22 h. The first product was a very fine bright orange powder from the cooled reaction mixture. The filtrate dried to a crust and when MeOH was added to this most dissolved to form a yellow solution. The undissolved material was bright yellow micro-crystals. Examination of the IRs (Table 6·10), FAB-ms (Table 6·11) and the analyses of both these products show them to be the same and they were combined as complex **71**. $[Mn_4\mathbf{LV5}Cl_7]\cdot 3H_2O$ (another $Mn^{II}Mn^{III}_3$ product) is a possible formula for **71** as it gives a close match to the chemical analysis of this product and no evidence for a central oxygen moiety is seen in the FAB-ms. However, this is formulation is not supported by the colour. The macrocyclic ligand is bright yellow and this is thought to be the source of the colour of complex **71** implying that the manganese ions are all colourless Mn(II). The $MnCl_4^{2-}$ anion is greenish-yellow if tetrahedral and pink if

polymeric octahedral with halide bridges[232]. Such bridged macrocyclic complexes are likely (particularly with chloride anions) of the **LV5** ligand. Consequently the formula $[Mn_4\mathbf{LV5}Cl_2]\cdot MnCl_4^{2-}\cdot 2H_2O$, in which all the metal ions are Mn^{II}, has been assigned to **71**.

Table 6·11 : Selected FAB-ms ions for LV5 - Cl complexes

LV5 + Cl		70	71
LV5, 6Mn, 6Cl, OH	1045·7	1047	
LV5, 4Mn, 4Cl, H_2O	866·2		865·9
LV5, 4Mn, O, 3Cl	830·7	829	
LV5, 4Mn, 3Cl	814·7	815	
LV5, 4Mn, O, 2Cl	793·9	794	
LV5, 4Mn, O, Cl	758·0	759	
H_2**LV5**, 2Mn, 3Cl, OH	722·0	724	
H_2**LV5**, 2Mn, 2Cl	670·1	671	671·0
H_2**LV5**, 2Mn, Cl	635·9	635	635·0
H_2**Lo-s**, Mn, O	478·1		478·0

The reactions with **LV5t** carried out with and without the presence of TEA both produced powders which contain tetranuclear products and some other material. These are complexes **72** $[Mn_4\mathbf{LV5t}Cl_5]\cdot MnCl_4^{2-}\cdot 3H_2O\cdot CH_3OH$ and **73** $[Mn_4\mathbf{LV5t}Cl_6]\cdot 2Mn_2Cl_4\cdot 4H_2O\cdot 2CH_3OH$ (Table 6·9). Both reaction mixtures were dark brown, the refluxing times were 22h and 25 h respectively and, like the **LV5** reactions with chloride, the products were collected directly from the cooled reaction mixtures. No peaks seen in the FAB-ms spectra of these complexes (Table 6·12) are for fragments which would indicate the inclusion of a μ-O moiety. Both products were greenish brown powders with the one from the reaction in which TEA was present (Complex **72**) having a slightly more yellow tinge. The above formulations assign **72** as a $Mn^{II}Mn^{III}_3$ complex and **73** as $Mn^{II}_2Mn^{III}_2$ and this is supported by their colours.

Table 6·12 : Selected FAB-ms ions for LV5t - Cl complexes

LV5t + Cl		72	73
LV5t, 4Mn, 4Cl,	878·0	878·0	
H**LV5t**, 3Mn, 3Cl	843·1	843·0	843
H**LV5t**, 3Mn, 2Cl	808·1	808·0	808
H**LV5t**, 3Mn, OH	755·1	755·1	755
H_2**LV5t**, 2Mn, Cl	719·2	719·1	719
H**LV5t**, 2Mn	683·2	683·1	683
H_3**LV5t**, Mn	630·3	630·2	
H_2**Lo-st**, Mn	548·2		548

5 : THE NITRATE COMPLEXES

Table 6·13 : Nitrate complexes of LV5 and LV5t

74	$[Mn_2(H_4\mathbf{LV5})(OH)Cl(NO_3)_2]\cdot H_2O$
75	$[Mn_4\mathbf{LV5}(NO_3)_2Cl_4]\cdot Mn_2Cl_4^{2-}\cdot 3CH_3CH_2OH$
76	$[Mn_4\mathbf{LV5t}Cl(NO_3)_4]\cdot CH_3OH\cdot CH_3CH_2OH$

Table 6·13 shows the three complexes identified from the reactions between manganese nitrate and the **LV5** and **LV5t** ligands. The analysis of complex **74** $[Mn_2(H_4\mathbf{LV5})(OH)Cl(NO_3)_2]\cdot H_2O$ shows it to be a binuclear product but ions for a trace of a tetranuclear complex can be seen in the FAB-ms (Table 6·14). Addition of TEA to another reaction mixture resulted in the formation of a browny-orange solid (complex **75** $[Mn_4\mathbf{LV5}(NO_3)_2Cl_4]\cdot[Mn_2Cl_4\cdot 3CH_3CH_2OH]$) which was filtered from the deep brown reaction mixture after 20 h of refluxing.

Table 6·14 : Nitrate complexes of LV5 and LV5t and selected IR frequencies (cm-1)

74	3395	2922	1651		1538	1384	965		857	813
75	3401	2919		1629	1557	1384	967			825
76	3415	2950	1653	1626	1537	1384		866		825

Complex **76** $[Mn_4\mathbf{LV5t}Cl(NO_3)_4]\cdot CH_3OH\cdot CH_3CH_2OH$ was the only **LV5t** - NO_3 identified. The reaction mixture was refluxed overnight after which time a solid was visible around the solvent line. This yellow-orange feathery material was collected by vacuum filtration. Ions for tetranuclear products dominate (Table 6·15) the FAB-ms and the above formula has excellent agreement with the chemical analysis. This means that this is a $Mn^{II}_3Mn^{III}$ complex and thus completes the redox series.

Table 6·15 : Selected FAB-ms ions for LV5t & LV5 - Cl complexes

LV5 & LV5t + NO_3		**74**	**75**	**76**
LV5, 4Mn, Cl, OH, NO_3	822·0	823·2		
H**LV5**, 3Mn, $2NO_3$, H_2O	796·4	796·1		
H_2**LV5**, 2Mn, 2Cl	670·1	671·1		
H_2**LV5**, 2Mn, Cl	635·1	635·1		
H_2**LV5**, 2Mn	600·1		599·1	
H_4**LV5**	492·6		494·1	
Lo-s, Mn, O	478·1		478·1	
LV5t, 4Mn, NO_3, 2Cl, OH	942·4			942·0
LV5t, 4Mn, $2NO_3$	916·5			917·0
LV5t, 4Mn, 3Cl	898·9			898·9
H**LV5t**, 3Mn, OH	755·6			757·0
H_2**LV5t**, 2Mn, Cl	719·2			719·0

6 : CONCLUSION

Tetranuclear manganese complexes have been synthesised and it appears that all but one (i.e. $Mn^{II}_3Mn^{III}$) of the series of mixed redox state complexes has been completed. When the acetate anion was used tetranuclear complexes and binuclear complexes of both the full and open-sided ligands resulted. Only binuclear complexes have resulted when the perchlorate anion was used and this may be related to the less coordinating nature of this anion. In contrast only tetranuclear products are seen when chloride is the anion. With only three nitrate complexes identified it would be imprudent to comment on a trend.

Mn^{II}_4	*	$Mn^{II}_2Mn^{III}_2$	$Mn^{II}Mn^{III}_3$	Mn^{III}_4

The orange coloured complex **71** $[Mn_4\mathbf{LV5}Cl_2]\cdot MnCl_4^{2-}\cdot 2H_2O$ contains only colourless Mn^{II} ions and a second $Mn^{II}_2Mn^{III}_2$ complex (**75**) has been synthesised. Most of the mixed valence complexes are thought to be $Mn^{II}Mn^{III}_3$ (e.g. **56** $[Mn_4(\mu_4\text{-}O)\mathbf{LV5}Cl(CH_3COO)_4]\cdot CH_3OH\cdot 5H_2O$). One complex **62** $[Mn_4\mathbf{LV5}(CH_3COO)_2(CH_3COOH)_2Cl_4][Mn_2Cl_4\cdot 3H_2O]\cdot 2H_2O$ is thought to contain all Mn^{III} ions.

Of the remaining large number of manganese reaction products not discussed here many of them appear to be complex mixtures of polymeric materials (in small amounts) and macrocyclic complexes. The most difficult part of this project has been to get totally clean samples. Even when the reaction products are homogenous (as indicated by repeatable microanalysis results) it appears that many are mixtures containing at least traces of a second component. This is thought to be a reason for being unable to obtain suitable crystals from the myriad of approaches tried. Structural characterisation of the redox series is obviously the most important next step of this project and it is thought that this is only going to be achieved with pure samples. The differing solubilities of the various macrocyclic forms appears to be the key to the separation of these and future work should be directed to a closer examination of this possibility. It is likely that column chromatography may be the answer to this problem.

EXPERIMENTAL - MANGANESE COMPLEXES

1 : MANGANESE WITH ACETATE

LV5 complexes

Complex 56 : $[Mn_4(\mu_4\text{-}O)LV5Cl(CH_3COO)_4]\cdot CH_3OH\cdot 5H_2O$

$Mn(CH_3COO)_2.4H_2O$ (4 mmol, 0·980 g) and 2,6-diformyl-4-methylphenol (2 mmol, 0·324 g) was dissolved in boiling dry ethanol (50mL). The brown solution was refluxed for 10 min. While continuing to reflux a solution of 1,5-diamino-3-hydroxypentane made from the dihydrochloride salt (2 mmol, 0·382 g) neutralised with KOH (4 mmol, 0·224 g) in dry methanol was added dropwise with constant stirring. The dark brown solution was refluxed for 24 h and allowed to cool slowly, while stirring, over 3 days. The almost black solution was transferred to a beaker and after 10 days had reduced to a black oil covered with a crust. This was redissolved in MeOH and half retained in a capped vial and the rest set up as a number of aliquots for ether diffusion. Eventually a tiny amount of black powder, a few black crystals (Complex **56**), and a small sample of dark brown powder (Complex **57**) were retrieved from these.

Yield : 0·015g, 0·0134 mmol, 1·34%

IR :3414, 2913, 2853, 1662, 1645, 1629, 1566, 1414, 968, 891, 822, 768 cm^{-1}

FAB-ms : 993·1(1), 960·0(5), 936·0(7), 915·0(2), 901·0(78), 877(30), 842·0(100), 817·9(23), 780·9(67), 756·9(26)

995·1 : **LV5**, 4Mn, O, 4OAc, Cl
960·0 : **LV5**, 4Mn, O, 4OAc
936·0 : **LV5**, 4Mn, O, 3OAc, Cl
917·0 : **LV5**, 4Mn, O, 3OAc, O
901·0 : **LV5**, 4Mn, O, 3OAc
885·0 : **LV5**, 4Mn, 3OAc
842·0 : **LV5**, 4Mn, O, 2OAc all peaks for tetranuclear products

Analysis for : $[Mn_4(\mu_4\text{-}O)$**LV5**$Cl(CH_3COO)_4]\cdot CH_3OH\cdot 5H_2O$

Calculated :	C : 39·75;	H : 5·23;	N : 5·01 %
Found :	C : 39·52;	H : 5·12;	N : 5·11 %

57 : $[Mn_4LV5(CH_3COO)_4Cl_3]$ + $[Mn_2(H_2Lo\text{-}s(CH_3COO)]\cdot 2CH_3CH_2OH$

This product was collected from the same reaction as **56**

Yield : 0·088 g, 0·0511 mmol, 5·11%

IR: 3474, 2915, 2283, 1661, 1623, 1548, 1453, 1394, 960, 891, 763, 744 cm^{-1}

FAB-ms(solid) : 1203(1), 1187(8), 1093·2(2), 1067(4), 1051·2(44), 980·2(1), 887·1(2), 874·1(3), 860·1(1), 820·1(4), 804·0(14), 777·0(7), 728·1(3), 706·0(6), 588·0(55), 577·0(34), 517·0 (64), 464·1(36).

Analysis for : $[Mn_4\mathbf{LV5}(CH_3COO)_4Cl_3]$ + $[Mn_2H_2\mathbf{Lo\text{-}s}(CH_3COO)]\cdot 2CH_3CH_2OH$

Calculated :	C : 46·93;	H : 4·97;	N : 5·05 %
Found :	C : 47·19;	H : 4·87;	N : 4·30 %

Complex 58 : $[Mn_2(H_3Lo\text{-}s)Cl_2]\cdot MnCl_4^{2-}\cdot CH_3OH\cdot 2H_2O$

The residue from **56** and **57** was redissolved in MeOH and set up in six portions for ether diffusion. Eventually a brown powder **58** was collected from these.

Yield : 0·097 g, 0·1124 mmol, 11·24 %.

IR: 3410, 2929, 2860, 1665, 1624, 1549, 1452, 1396, 958, 881, 763, 745 cm^{-1}

FAB-ms(solid) : not much better - 673·2(1), 633(3), 629·2(3), 497·1(7), 480·0(9), 464·0(100).

Analysis : $[Mn_2(H_3\mathbf{Lo\text{-}s})Cl_2]\cdot MnCl_4^{2-}\cdot CH_3OH\cdot 2H_2O$

Calculated :	C : 33·67;	H : 4·00;	N : 3·27 %
Found :	C : 33·54;	H : 4·37;	N : 3·35 %

Complex 59 :

$[Mn_4LV5Cl_2(CH_3COO)_3(CH_3COOH)]\cdot MnCl_4^{2-}\cdot 2CH_3CH_2OH\cdot CH_3OH\cdot 2H_2O$

The manganese acetate (4 mmol, 0·926 g) and dfmp (2 mmol, 0·324 g) were dissolved in 40mL hot dry 1 : 1 methanol : ethanol and the solution refluxed for 10 min. A solution of dahp was made, from the dihydrochloride salt (2 mmol, 0·382 g) neutralised with KOH (4 mmol, 0·224 g), in 20 mL of dry 1 : 1 MeOH : EtOH. This solution was added dropwise, with constant stirring, through filter paper at the top of the condenser. The deep yellow-brown solution was refluxed for 48 h, allowed to cool, and left stoppered over the weekend. The solution was let evaporate slowly for 12 days and a few tiny dark brown crystals appeared around the solvent line. The filtrate was heated to boiling, ether

added, and the mixture left to evaporate slowly. After a considerable period of time dark brown flaky material was collected from this.

Yield : 0·632 g, 0·465 mmol, 46·47 %.

IR : 3409, 2924, 1628(pre sh), 1569, 1427, 1322, 961, 890, 822, 770 cm^{-1}.

FAB-ms : 1047·0(16), 953·9(10), 929·8(9), 900·8(44), 875·8(42), 841·8(96), 817·8(27), 800·8(22), 782·8(96), 758·8(100), 740·8(73),719(34).

Analysis for :
$[Mn_4\mathbf{LV5}Cl_2(CH_3COO)_3(CH_3COOH)]\cdot MnCl_4^{2-}\cdot 2CH_3CH_2OH\cdot CH_3OH\cdot 2H_2O$

Calculated :	C : 35·32;	H : 4·74;	N : 4·12 %
Found :	C : 35·50;	H : 4·61;	N : 3·68 %

Complex 60 : $[Mn_4LV5Cl_3(CH_3COO)_4]\cdot CH_3CH_2OH\cdot 3H_2O$

Some solid from **59** was dissolved in CH_2Cl_2 and eventually yielded some pale brown powder - complex **60**.

Yield : 0· g, 0· mmol, %.

IR : 3415, 1625, 1558, 1448, 1405, 963, 892, 823, 766 cm^{-1}.

FAB-ms : 977·6(18),841·9(17), 827·9(24), 817·9(16), 782·8(30), 768·8(26), 758·8(37), 740·9(33), 637(60), 599·0(63), 487·9(54), 464·0(100)

Analysis for : $[Mn_4\mathbf{LV5}Cl_3(CH_3COO)_4]\cdot CH_3CH_2OH\cdot 3H_2O$

Calculated :	C : 39·65;	H : 4·90;	N : 5·07 %
Found :	C : 39·33;	H : 4·62;	N : 4·46 %

Complex 61 : $[Mn_2H_2Lo\text{-}s(2\cdot5Cl)(CH_3COO)(0\cdot5OH)]$

The manganese acetate (4 mmol) and dfmp (2 mmol) were mixed in 100mL dry EtOH and the golden yellow solution refluxed 25 mins. A 2 mmol dahp solution was added dropwise and a golden brown solution formed. 1 mL of TEA (a little over 6 mmol) was added dropwise and the reaction mixture refluxed with stirring overnight. After cooling the dark brown reaction mixture yielded a tiny amount of very dark brown powder.

Yield : 0·015 g, 0·023 mmol, 2·30 %.

IR : 3401, 2921, 1629, 1554, 1448, 1418, 1105, 975, 829, 812, 773 cm^{-1}.

FAB-ms : 865(10), 850·4(16), 783·3(20), 743·4(13), 719·3(25), 699·3(19), 683·4(100), 599·2(47), 570·2(45), 514·2(40)

Analysis for : $[Mn_2H_2$**Lo-s**$(2{\cdot}5Cl)(CH_3COO)(0{\cdot}5OH)]$

Calculated :	C : 44·45;	H : 4·25;	N : 4·15 %
Found :	C : 44·42;	H : 4·24;	N : 4·16 %

Complex 62 : $[Mn_4$LV5$(CH_3COO)_2(CH_3COOH)_2Cl_4][Mn_2Cl_4{\cdot}3H_2O]{\cdot}2H_2O$

The filtrate of **61** was evaporated to dryness and mixed with EtOH. The dark brown microcrystalline material was collected by vacuum filtration.

Yield : 0·684 g, 0·4925 mmol, 49·25%.

IR: 3422, 2929, 1667, 1625, 1602, 1550, 1452, 1398, 959, 834, 764, 745 cm^{-1}

FAB-ms : 876·0(13), 842·1(14), 818·0(9), 759(41), 659·1(60), 635·1(62), 599·1(77), 539·2(65), 497 (100), 486·0(52), 464(81), 429·1(), 404·0().

FAB-ms(solid) : 1051·1(6), 901·1(39), 875·9(5), 842·0(66), 782·9(74), 766·9(9), 728·0(16), 682·0(29), 659·0(37), 576·9(100), 559·3(20), 542(35), 516·9(65), 497·1(67).

Analysis for : $[Mn_4$**LV5**$(CH_3COO)_2(CH_3COOH)_2Cl_4][Mn_2Cl_4{\cdot}3H_2O]{\cdot}2H_2O$

Calculated :	C : 30·24;	H : 3·92;	N : 3·92 %
Found :	C : 29·82;	H : 3·77;	N : 2·89 %

LV5t Complexes

Complex 63 : $[Mn_4$LV5t$(dftp)_2Cl_2(OH)_2]{\cdot}CH_3OH$

The manganese acetate (4 mmol) and dftp (2 mmol) were mixed in 50mL dry MeOH and the golden yellow solution refluxed 2 h. A 2 mmol dahp solution was added rapidly and a brown suspension formed. 1 mL of TEA (a little over 6 mmol) was added dropwise and the reaction mixture refluxed with stirring 24 h. After cooling overnight the dark brown reaction mixture yielded a tiny amount of pale yellow-brown powder.

Yield : 0·014 g, 0·0104 mmol, 1·04 %.

IR : 3426, 2960, 1629, 1549, 1451, 1419, 1384, 1268, 842, 816, 737 cm^{-1}.

FAB-ms : 1045·8(8), 1028·1(16), 1016·2(12), 982·9(21), 960·0(14), 926·1(24), 867·0(55), 743·1(32), 683·1(90), 598·0(44), 570·0(86), 459·0(100) - polymeric in lower range - not much above background.

Analysis for : $[Mn_4$**LV5t**$(dftp)_2Cl_2(OH)_2]{\cdot}CH_3OH$

Calculated :	C : 52·81;	H : 5·86;	N : 4·18 %
Found :	C : 52·60;	H : 5·60;	N : 4·29 %

2 : MANGANESE WITH PERCHLORATE

LV5 Complexes

The manganese perchlorate (4 mmol, 1·448 g) and dfmp (2 mmol, 0·324 g) were dissolved in 50mL hot dry ethanol and the golden solution was refluxed for 10 min. A solution of dahp was made, from the dihydrochloride salt (2 mmol, 0·382 g) neutralised with KOH (4 mmol, 0·224 g), in 20 mL of dry 1 : 1 MeOH : EtOH. This solution was added dropwise, with constant stirring, through filter paper at the top of the condenser. The deep yellow-brown solution was refluxed for 24 h and allowed to cool slowly while still stirring. A yellowish-brown powder was collected from the dark brown solution.

Yield : 0·238 g, 0·150 mmol, 15·00 %.

IR : 3422, 2925, 1654, 1540, 1087, 940, 867, 814, 625 cm^{-1}.

FAB-ms : 735·1(50), 699·1(53), 673(26), 635·1(100), 599(17), 564·1(34), 546·1(30), 464·1(80), 418(33).

Analysis indicates this is a mixture of a macrocyclic product and metal salt.

Complex 64 : $[Mn_2(H_4LV5)Cl_3(ClO_4)]\cdot 2H_2O\cdot CH_3CH_2OH$

The filtrate of the above mixture was set aside and overnight more brownish yellow powder had formed in this.

Yield : 0·014 g, 0·016 mmol, 1·60 %.

IR : 3439, 2925, 1661, 1539, 1108, 872, 625 cm^{-1}.

FAB-ms : 699·1(3), 662·1(2), 643(2), 617·1(1), 564·1(15), 493·2(19), 464·1(100).

Analysis for : $[Mn_2(H_4\mathbf{LV5})Cl_3(ClO_4)]\cdot 2H_2O\cdot CH_3CH_2OH$

Calculated :	C : 40·56;	H : 4·99;	N : 6·31 %
Found :	C : 40·97;	H : 4·67;	N : 6·42 %

Complex 65 : $[Mn_2(H_4LV5)Cl_2(ClO_4)(CH_3CH_2O)]$

The filtrate was reduced under vacuum and aliquots of this solution were set up for ether diffusion. After 7 days each of these contained some solid so the liquid was decanted off, all of the solids were combined and stirred in dry MeOH, and undissolved solid (a yellow-brown cake) collected.

Yield : 0·099 g, 0·1214 mmol, 12·14 %.

IR : 3424, 2924, 1653, 1534, 1098, 870, 625 cm^{-1}.

FAB-ms : 763·3(6), 699·2(10), 599·2(7), 564·2(20), 546·3(8), 493·3(33), 464·2(100).

Analysis for : $[Mn_2(H_4\mathbf{LV5})Cl_2(ClO_4)(CH_3CH_2O)]$

Calculated :	C : 44·11;	H : 4·96;	N : 6·86 %
Found :	C : 44·21;	H : 4·86;	N : 6·56 %

Complex 66 : $[Mn_2(H_4LV5)(ClO_4)Cl_3]\cdot 2H_2O\cdot CH_3OH$

The filtrate of **65** was divided into 6 aliquots and set up for ether diffusion and an orangey-brown powder was retrieved from all of these. Samples of this were dissolved in N,N-dimethylacetamide, dmf, and ethyl acetate. Some microcrystalline material was collected from the ethyl acetate portions.

IR : 3427, 3230, 2924, 1663, ~1630, 1533, 1096, 987, 870, 818, 624 cm^{-1}.

FAB-ms : 735(11), 699·1(42), 671·1(13), 635·1(54), 599·1(28), 564·1(24), 546(14), 495(33), 488·0(18), 464·1(100).

Analysis for : $[Mn_2(H_4\mathbf{LV5})(ClO_4)Cl_3]\cdot 2H_2O\cdot CH_3OH$

Calculated :	C : 39·84;	H : 4·84;	N : 6·41 %
Found :	C : 39·99;	H : 4·79;	N : 6·31 %

Complex 67 : $[Mn_2(H_4LV5)(ClO_4)_2(OH)_2]\cdot CH_3CH_2OH$

The solutions were made in 1 : 1 MeOH : EtOH with 20 mL being used for the dahp and 40 mL for the metal-dfmp solutions. 2 mmol of $Mn(ClO_4)_2$ was used in the hope that a binuclear complex would form. After refluxing 23 h the dark brown solution was allowed to cool to room temperature. After 2 days a very fine tan coloured powder was collected from the reaction mixture.

Yield : 0·261 g, 0·6946 mmol, 69·46%.

IR : 3407, 2923, 1663, 1640, 1529, 1122, 1079, 990, 872, 625 cm^{-1}.

FAB-ms : 857(22), 840(17), 766(27), 739(28), 710(15), 699(37), 664(15), 599(28), 564(53), 493(58), 464(100).

UV : ~450, ~350(slight)

Analysis for : $[Mn_2(H_4\mathbf{LV5})(ClO_4)_2(OH)_2]\cdot CH_3CH_2OH$

Calculated :	C : 41·07;	H : 4·59;	N : 6·39 %
Found :	C : 40·89;	H : 4·60;	N : 6·25 %

Complex 68 : $[Mn_2(H_4LV5)(ClO_4)_3Cl_2]\cdot 2\cdot 5CH_3CH_2OH$

The filtrate of **67** was allowed to evaporate slowly and after considerable time yielded a khaki powder and a few black crystals which were not suitable for X-ray analysis.

Yield : 0·459 g, 0·4334 mmol, 43·34%.

IR : 3406, 3223, 1667, 1627, 1560, 1088, 958, 896, 847, 818, 763, 718, 625 cm^{-1}.

FAB-ms : 866(5), 802(10), 767(8), 735(8), 698(9), 635(14), 598(11), 564(15), 500(28), 464(100).

UV : ~450, ~350

Analysis for : $[Mn_2(H_4\mathbf{LV5})(ClO_4)_3Cl_2]\cdot 2\cdot 5CH_3CH_2OH$

Calculated :	C : 36·53;	H : 4·55;	N : 5·16 %
Found :	C : 36·62;	H : 4·23;	N : 4·87 %

LV5t Complexes

Complex 69 : $[Mn_2(H_4LV5t)(ClO_4)_4Cl]\cdot CH_3CH_2OH\cdot 3H_2O$

The manganese perchlorate (4 mmol) and dftp (2 mmol) were refluxed in dry EtOH for 25 mins. A 2 mmol dahp solution was added dropwise and the solution immediately went brown. The reaction mixture was refluxed without stirring 25 h. The 0·238 g of pale yellow solid which was collected from this reaction mixture was shown to be inorganic only. The dark brown filtrate was set aside for slow evaporation and when it had dried completely dry MeOH was added. The dark moss-green solid which didn't dissolve was collected by vacuum filtration.

Yield : 0·154 g, 0·1265 mmol, 12·65 %.

IR : 3364, 3236, 2953, 2866, 1659, 1624, 1556, 1454, 1082, 976, 899, 843, 775, 621 cm^{-1}.

FAB-ms : 819·3(36), 783·3(59), 755·3(18), 730·4(27), 719·3(100), 683·3(35), 630·4(55), 570·2(30)

Analysis : $[Mn_2(H_4\mathbf{LV5t})(ClO_4)_4Cl]\cdot CH_3CH_2OH\cdot 3H_2O$

Calculated :	C : 35·44;	H : 4·96;	N : 4·52 %
Found :	C : 35·53;	H : 4·96;	N : 4·52 %

3 : MANGANESE WITH CHLORIDE

LV5 Complexes

Complex 70 : $[Mn_4(\mu_4\text{-}O)LV5Cl_5]\cdot H_2O\cdot CH_3OH$

$MnCl_2$ (4 mmol, 0·792 g) and 2 mmol of dfmp was dissolved in hot dry EtOH and the pale yellow solution was refluxed for 20 mins. A 2mmol solution of dahp was added dropwise followed by 1 mL of (a little over 6 mmol) of TEA. The brown reaction mixture was refluxed for 22 h and cooled to room temperature overnight. A very fine dark greeny-brown powder was collected in a Hirsch funnel.

Yield : 0·654 g, 0·6331 mmol, 63·31 %.

IR : 3320, 2905, 2834, 2730, 1637, 1551, 1233, 1128, 971, 898, 877, 811, 772 cm^{-1}.

FAB-ms : 1082(15), 1047(12), 930(19), 829(28), 815(12), 794(88), 759(100), 724(16), 689(10), 671(33), 635(66), 584(18), 550(8), 470(8), 460(15).

Analysis for : $[Mn_4(\mu_4\text{-}O)\mathbf{LV5}Cl_5]\cdot H_2O\cdot CH_3OH$

Calculated :	C : 36·60;	H : 4·09;	N : 5·89 %
Found :	C : 36·55;	H : 3·98;	N : 5·70 %

Complex 71 : $[Mn_4LV5Cl_2]\cdot MnCl_4^{2-}\cdot 2H_2O$

$MnCl_2$ (4 mmol, 0·792 g) and 2 mmol of dfmp was dissolved in 50 mL hot dry EtOH and the pale yellow solution was refluxed for 20 mins. A 2 mmol solution of dahp was added dropwise while refluxing and stirring and an orange solid formed almost immediately. The reaction mixture was refluxed for 22 h, the bright orange very fine powder was collected by vacuum filtration and washed with 3 x 10 mL dry EtOH.

Yield : 0·541 g, 0·4959 mmol, 49·59 %.

IR : 3398, 3304, 3030, 2918, 1651, 1535, 1232, 865, 812, 779, 668 cm^{-1}.

FAB-ms : 865·8(20), 671·0(52), 635·0(100), 478·0(74).

Analysis for : $[Mn_4\mathbf{LV5}Cl_2]\cdot MnCl_4^{2-}\cdot 2H_2O$

Calculated :	C : 33·23;	H : 3·59;	N : 5·54 %
Found :	C : 33·25;	H : 3·78;	N : 5·45 %

The filtrate which had dried to a brown and yellow crust. Dry MeOH was added and most dissolved to a golden brown solution. A tiny amount of bright yellow microcrystalline material was collected.

Yield : 0·0237 g, 0·0217 mmol, 2·17 %.

IR : 3308, 2919, 1652, 1538, 1497, 1232

FAB-ms : 1207(15), 865·8(23), 671·0(53), 635·0(100), 528·1(20), 478·0(73).

Analysis for : $[Mn_4\mathbf{LV5}Cl_2]\cdot MnCl_4^{2-}\cdot 2H_2O$

Calculated :	C : 33·23;	H : 3·59;	N : 5·54 %
Found :	C : 33·11;	H : 3·77;	N : 5·47 %

Since the second product is shown to be the same as the first the two were combined - overall yield - 51·76 %.

Complex 72 : $[Mn_4\mathbf{LV5t}Cl_5]\cdot MnCl_4^{2-}\cdot 3H_2O\cdot CH_3OH$

$MnCl_2$ (4 mmol, 0·792 g) and 2 mmol of dfmp was dissolved in hot dry EtOH and the pale yellow solution was refluxed for 20 mins. A 2 mmol solution of dahp and then 1 mL (a little over 6 mmol) of TEA, was added dropwise with stirring. The brown reaction mixture was refluxed for 22 h and cooled to room temperature overnight. A greeny-yellow brown powder was collected in a Hirsch funnel.

Yield : 0·556 g, 0·4317 mmol, 43·17 %.

IR : 3404, 2956, 2865, 1626(spl), 1554, 1095, 972, 895, 842, 780, 765 cm^{-1}.

FAB-ms(solid) : 1166·1(4), 1131·1(7), 1014·0(10), 995·1(7), 917(10), 878·0(22), 843·0(52), 808·0(20), 825·1(18), 788·1(26), 772·1(28), 755·2(40), 719·2(100), 570·1(100).

Analysis for : $[Mn_4\mathbf{LV5t}Cl_5]\cdot MnCl_4^{2-}\cdot 3H_2O\cdot CH_3OH$

Calculated :	C : 33·56;	H : 4·35;	N : 4·47 %
Found :	C : 33·58;	H : 4·48;	N : 4·50 %

Complex 73 : $[Mn_4\mathbf{LV5t}Cl_6]\cdot 2Mn_2Cl_4\cdot 4H_2O\cdot 2CH_3OH$

$MnCl_2$ (4 mmol, 0·792 g) and 2 mmol of dfmp was dissolved in hot dry EtOH and the pale yellow solution was refluxed for 25 mins. A 2 mmol solution of dahp was added dropwise and the brown reaction mixture was refluxed, without stirring, for 25 h. The reaction mixture was cooled to room temperature and sat

for 3 days after which time a greenish brown powder was collected under vacuum filtration.

Yield : 0·165 g, 0·1262 mmol, 12·62 %.

IR : 3372, 3212, 2957, 1657, 1627, 1554, 1093, 842, 778, 757 cm^{-1}.

FAB-ms : 843(10), 808(15), 755(50), 719(100) - mostly polymeric looking

Analysis for : $[Mn_4\mathbf{LV5t}Cl_6]\cdot 2Mn_2Cl_4\cdot 4H_2O\cdot 2CH_3OH$

Calculated :	C : 26·29;	H : 3·68;	N : 3·41 %
Found :	C : 26·17;	H : 3·45;	N : 3·18 %

4 : MANGANESE WITH NITRATE

With LV5

Complex 74 : $[Mn_2(H_4LV5)(OH)Cl(NO_3)_2]\cdot H_2O$

$Co(NO_3)_2$ (4 mmol, 1·164 g) and dfmp (2 mmol) were dissolved in 50 mL dry EtOH and the pale yellow solution refluxed for 10 mins. A 2 mmol dahp solution was added dropwise and the deep brown solution refluxed overnight after which time an orange solid was visible in the now deep green solvent. The reaction mixture was left to sit 1 day. The browny-orange solid was collected under vacuum and washed with distilled H_2O.

Yield : 0·247 g, 0·3182 mmol, 31·82 %

IR : 3415, 3184, 2924, 1651, 1624, 1537, 1387, 1089, 996, 965, 930, 856, 813, 791, 775, 694 cm^{-1}.

FAB-ms : 823·2(10), 796·1(24), 765·1(17), 671·1(37), 635·1(100), 598·1(30), 478·1(76), 464·1(54).

Analysis for : $[Mn_2(H_4\mathbf{LV5})(OH)Cl(NO_3)_2]\cdot H_2O$

Calculated :	C : 42·30;	H : 4·84;	N : 10·57 %
Found :	C : 42·01;	H : 4·65;	N : 10·47 %

Complex 75 : $[Mn_4LV5(NO_3)_2Cl_4]\cdot Mn_2Cl_4\cdot 3CH_3CH_2OH$

$Co(NO_3)_2$ (4 mmol, 1·164 g) and dfmp (2 mmol) were dissolved in 50 mL dry EtOH and the pale yellow solution refluxed for 15 mins. A 2 mmol dahp solution was added dropwise to produce an orange solution. I mL TEA (a little over 6 mmols) was added dropwise and an orange solid formed immediately.

The brown reaction mixture was refluxed for 24 h and left to cool for 2 days after which time a little brown powder and a lot of white needle-like crystals were collected. The crystals (probably KCl) dissolved in water and the remaining dark brown powder was washed with 3 x 5mL of H_2O. The dark brown filtrate was set aside.

Yield : 0·068 g, 0·0492 mmol, 4·92 %.

IR : 3401, 2920, 1627, 1557, 1384(sharp), 1095, 967, 825 cm^{-1}.

FAB-ms : 599·1(9), 494·1(19), 478·1(30).

Analysis for : $[Mn_4\mathbf{LV5}(NO_3)_2Cl_4]\cdot Mn_2Cl_4\cdot 3CH_3CH_2OH$

Calculated :	C : 29·94;	H : 3·69;	N : 6·16 %
Found :	C : 29·94;	H : 3·47;	N : 6·18 %

Complex 76 : $[Mn_4LV5tCl(NO_3)_4]\cdot CH_3OH\cdot CH_3CH_2OH$

$Co(NO_3)_2$ (4 mmol, 1·164 g) and dftp (2 mmol, 0·412 g) were dissolved in 50 mL dry EtOH and the golden yellow solution refluxed for 10 mins. A 2 mmol dahp solution was added dropwise and the dark golden-brown solution refluxed overnight after which time an orange solid was visible around the solvent line of the deep orange solution. The yellow-orange feathery solid was collected under vacuum.

Yield : 0·345 g, 0·2992 mmol, 29·92 %.

IR : 3415, 2950, 1653, 1626, 1539, 1384(sharp), 1109(trip), 866, 825 cm^{-1}.

FAB-ms : 942·0(3), 898·9(2), 757·0(24), 719·0(100),

Analysis for : $[Mn_4\mathbf{LV5t}Cl(NO_3)_4]\cdot CH_3OH\cdot CH_3CH_2OH$

Calculated :	C : 38·51;	H : 4·72;	N : 9·71 %
Found :	C : 38·65;	H : 4·71;	N : 9·72 %

CHAPTER 7

THE NICKEL COMPLEXES

1 : INTRODUCTION

It would be expected that the nickel complexes would not be like the cobalt or manganese complexes just discussed. Square planar, tetragonal or octahedral coordination geometry is most common for nickel(II) and so it would be expected that nickel containing macrocyclic complexes would be planar and this has proved to be the case for those characterised by X-ray structure analysis. This also means that as the coordination sphere around the nickel is completed, depending on the charge on the ligand, the complexes are likely to be neutral rather than cationic and therefore more soluble in organic solvents but not in MeOH.

The nickel complexes of the **LV5** and **LV5t** ligand systems have been the most difficult to isolate and characterise. It would seem that the products are not neutral species as they are not easily isolated from the reaction medium. The IRs of most of the products from all of the preparations have looked extremely good and appear to show well formed ligands. However, in many cases chemical analyses, carried out in view of the appearance of the IR, show that there is little or no nitrogen present. The normal procedure, at the Otago Microanalytical laboratory, is to duplicate the analysis of any sample if it does not agree with the speculated composition sent in. If the duplicates agree, within experimental error, then no further analyses are carried out. In the situation where there is not this agreement the laboratory usually carries on the analyses until all of the sample is used. For complexes like those being synthesised in this project this has proved to be extremely helpful in both determining the purity as well as the formula of the samples sent. The results for the cases mentioned above, the duplicates were within very good agreement implying that these samples are homogenous. This does not preclude there being more than one macrocyclic complex present.

The IR spectra were similarly less conclusive than for complexes of the other metals discussed. A few show distinctive binuclear or tetranuclear patterns, based on those distinguished for the cobalt complexes, but for the most part the patterns did not show anything easily recognised.

Many of the FAB-ms showed almost no peaks above background even when the spectra were re-run on solid samples. This suggests insolubility. Ironically many of the worst ones were for the complexes for which analytical results, which were reasonably readily fitted to an acceptable macrocyclic structure, had been obtained.

Nickel complexes of acetate, nitrate and perchlorate salts have been prepared.

2 : THE ACETATE COMPLEXES

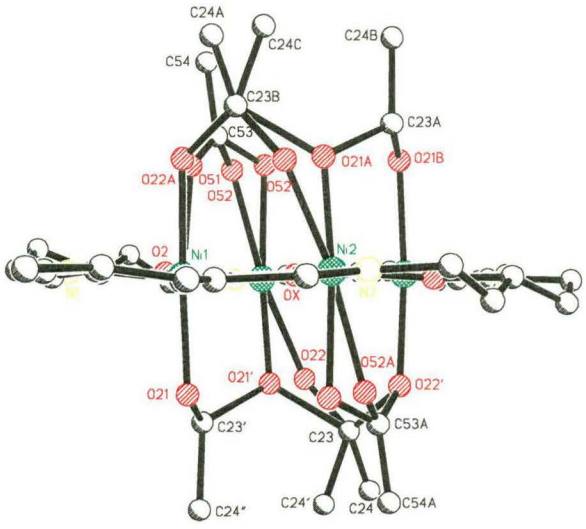


Figure 7·1 : The tetranuclear core of the nickel complex M21 showing only some of the considerable disorder exhibited by this structure.

Prior to the commencement of this project, crystals of a tetranuclear nickel - **LV5** complex (**M21**) in which the templating salt was nickel acetate, had been synthesised.[233] Characterisation by X-ray structure analysis showed the complex to be planar as expected, with four nickel ions coordinated within the plane and a central μ_4-OH^- (Fig. 7·1). A number of acetate ions are disordered

around the nickel ions and only some of their alternative positions are shown in Figure 7·1. Alternative positions were found for some of the macrocyclic carbons but these have not been shown. Refinement of the structure to acceptable values was not possible because of the considerable disorder it exhibited.

The synthesis using nickel acetate as the templating salt was repeated in this project and complexes **77** and **78** (refer p. 269) were isolated. Crystals of complex **79** were obtained from ether diffusion into a CH_2Cl_2 solution of complex **78**. Again it was revealed that the structure was tetranuclear, contained a μ_4-O species and was disordered. In this case even the nickel ions of the tetranuclear core exhibited rotational disorder (Fig. 7·2). It is difficult to pinpoint the source of the disorder. The structure has been solved in space group C_2 and it either does not have a 2-fold axis or it is twinned perpendicular to the 2-fold axis. It has not been possible to refine the structure at all.

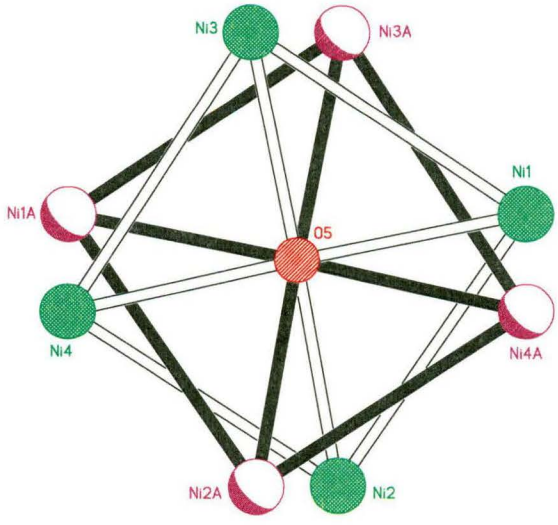


Figure 7·2 : The metal core of complex 2·1x

In a continuation of this work Paul Kruger has subsequently synthesised a tetranuclear nickel complex of **LV5t** (the *t*-butyl analogue of **LV5**).[222] This complex **M22** (Fig. 7·3) is planar and contains a μ_4-OH. The structure contains three bridging acetate groups and two coordinated acetic acid groups. On one face of the molecule an acetate bridges Ni4 and Ni1 while a second bridges Ni3 and Ni2. On the opposite face Ni3 and Ni4 are bridged by the third acetate and Ni1 and Ni2 have acetic acid groups coordinated to them.

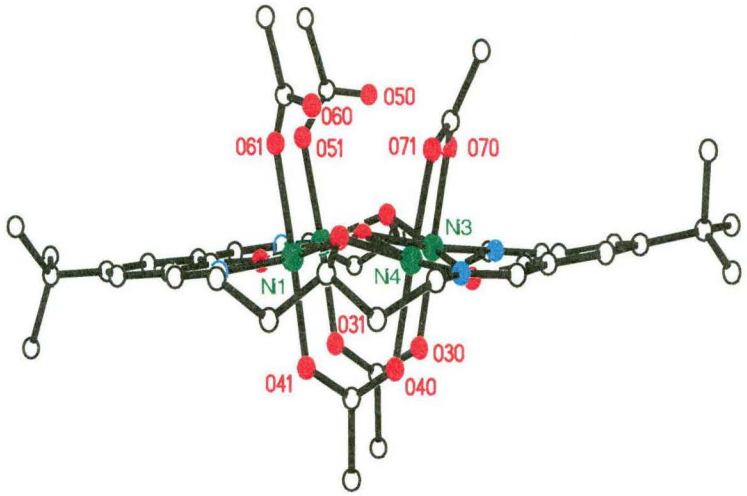


Figure 7·3 : The macrocyclic core of $[Ni_4LV5t(CH_3COO)_3(CH_3COOH)_2]\cdot DMF\cdot H_2O$

It would seem that complexes of **LV5t** are less soluble than **LV5** and consequently less difficult to isolate.

2·1 : Acetate complexes with LV5

Table 7·1 : Acetate complexes of LV5

77	$[Ni_4(\mu\text{-}OH)\mathbf{LV5}(CH_3COO)(CH_3COOH)_3]\cdot NiCl_4^{2-}\cdot CH_3CH_2OH\cdot H_2O$
78	$[Ni_4(\mu\text{-}OH)\mathbf{LV5}(CH_3COO)_3(CH_3COOH)]\cdot CH_3OH\cdot 3H_2O$
80	$[Ni_2(H_4\mathbf{LV5})(OH)(NCS)_3]\cdot 2H_2O$
81	$[Ni_2(H_4\mathbf{LV5})Cl_{1.5}(NCS)_{2.5}]\cdot CH_3OH$
82	$[Ni_2(H_4\mathbf{LV5})Cl(NCS)_3]$

Five **LV5** - nickel acetate complexes have been assigned formulae and these are shown in Table 7·1. Complexes **77** and **78** were isolated as light green powders and are assigned tetranuclear formulae. The IR spectra (Table 7·2) of complexes are exactly the same. Peaks for tetranuclear fragments containing μ-OH moieties (~796) are seen in the FAB-ms of both these complexes (Table 7·3) and the formulae shown are supported by the chemical analyses. It seems clear that the macrocyclic product is almost the same in each case. Complex **77** is formulated to contain the $NiCl_4^{2-}$ anion as complex chlorides are common with nickel and this anion forms readily in the presence of EtOH. However, this anion is blue and if it is present it might have been expected that the colour of **77** would be different to that of **78**.

Table 7·2 : Acetate complexes of LV5 with selected IR frequencies (cm^{-1})

77	3149	2909		1637	1593	1456	1405	883	852	820	774
78	3439	2916		1639	1599	1456	1406	883	853	820	773
80			2095	1642		1452		874		821	771
81	3384	2929	2095	1639	1542	1456		874		821	771
82	3407	2921	2093	1639		1497		872		822	771

Complex **77** was collected as a pale green powder from a bright green reaction mixture after 24 h of refluxing. The dfmp and $Ni(CH_3COO)_2$ had been dissolved in dry EtOH and the dahp in a MeOH/EtOH mixture. The volume of the filtrate was significantly reduced and eventually more powder product filtered off. Two lots of crystals were obtained when half of this powder was dissolved in CH_2Cl_2 and half in $CHCl_3$ and ether diffused in to these. In both cases although a data set was collected and a tetranuclear complex could be shown neither structure could be satisfactorily refined. Complex **79** has already been discussed.

A clean up procedure was employed before the isolation of complex **78** which was the final combined product from two reaction mixtures. In both of these syntheses the entire reaction was done in MeOH. In the first synthesis a green powder was filtered from the hot reaction mixture and a second green powder was filtered from the concentrated filtrate. Both contained visible white crystals (probably KCl). The second synthesis was carried out in the same way and yielded a light green powder and a further leaf green powder was collected from the filtrate. These were also contaminated with white crystals. As the IR spectra of all these products were essentially the same they were all combined, dissolved in CH_2Cl_2 and stirred. The white crystals did not dissolve and were filtered off. Chemical analysis agrees with the formulation of complex **78**as $[Ni_4(\mu\text{-}OH)\mathbf{LV5}(CH_3COO)_3(CH_3COOH)]\cdot CH_3OH\cdot 3H_2O$. The fact that these coloured powders dissolved so easily in CH_2Cl_2 supports their formulation as neutral species.

The three complexes which have been assigned binuclear formulas were recovered from two separate reactions in which samples of **78** were redissolved in MeOH, excess NH_4NCS added, and the mixtures stirred at room temperature for some hours. Complex **80** $[Ni_2(H_4\mathbf{LV5})(OH)(NCS)_3]\cdot 2H_2O$ was collected as a yellow powder from the first of these and identified by chemical analysis. No mass spectrum was done. Two products were collected from the second

reaction. Complex **81** $[Ni_2(H_4\mathbf{LV5})(OH)Cl(NCS)_3]\cdot 2CH_3CH_2OH$ was filtered from the reaction mixture after stirring and complex **82** $[Ni_2(H_4\mathbf{LV5})0{\cdot}5(OH)0{\cdot}5Cl(NCS)_3]\cdot H_2O$ from the filtrate.

Table 7·3 : Selected FAB-ms ions for LV5 - CH_3COO^- complexes

		77	78	81
LV5, 4Ni, 4OAc, Cl	991·00	992·9		
LV5, 4Ni, 2OAc, OH	855·01	856·7	855·8	
H_3**LV5**, 2Ni, 3NCS, Cl	816·03			816·19
LV5, 4Ni, OH, OAc	795·99	796·8	796·7	
LV5, 4Ni, OH_2	737·99	737·8	737·8	
H_4**LV5**, 2Ni, 3Cl	709·02		709	
H_4**LV5**, 2Ni, 2Cl	678·08	679·7	679	
H_4**LV5**, 2Ni, O, Cl	655·08	653·7	652·7	
H_4**LV5**	492·27	491·7	491·7	

2·2 : Acetate complexes with LV5t

A wide range of nickel acetate - **LV5t** syntheses were tried and the complexes for which formulae have been assigned are shown in Table 7·4. In all but one case complexes were isolated after the further addition of thiocyanate, perchlorate or azide, to the acetate reaction mixtures. Complexes **83**, **84**, and **85**, are thought to be tetranuclear while **86**, **87**, **88**, have been assigned binuclear formulae.

Table 7·4 : Nickel - Acetate complexes of LV5t

83	$[Ni_4(\mu\text{-}OH)\mathbf{LV5t}Cl_2(CH_3COO)(CH_3COOH)_2]\cdot 2CH_3OH\cdot CH_3CH_2OH$
84	$[Ni_4(\mu\text{-}OH)\mathbf{LV5t}(CH_3COO)_2(CH_3COOH)_3(ClO_4)]\cdot CH_3CH_2OH$
85	$[Ni_4(\mu\text{-}OH)\mathbf{LV5t}(N_3)_2Cl_2(CH_3COOH)]\cdot CH_3OH$
86	$[Ni_2(H_4\mathbf{LV5t})2Cl(NCS)_2]\cdot 1{\cdot}5CH_3CH_2OH$
87	$[Ni_2(H_4\mathbf{LV5t})Cl(NCS)_3]\cdot CH_3CH_2OH\cdot CH_3OH$
88	$[Ni_2(H_4\mathbf{LV5t})(NCS)_4]\cdot 2CH_3CH_2OH$

Table 7·5 : LV5t - OAc complexes - selected IR frequencies (cm-1)

83	3398	2953		1688	1637	1556		1412		
84	3422	2958		1685	1642	1560		1419	1121	623
85	3404	2958	2088		1643	1554	1457	1410		
86	3404	2959	2092	1653		1539	1457			
87	3405	2957	2093	1652		1538	1456			
88	3415	2957	2091	1653		1536	1459			

Complex **83** $[Ni_4(\mu\text{-}OH)\mathbf{LV5t}Cl_2(CH_3COO)(CH_3COOH)_2]\cdot 2CH_3OH\cdot CH_3CH_2OH$ came from a reaction in which the $Ni(CH_3COO)_2$ was refluxed with dftp in hot

MeOH and the dahp solution added in a MeOH/EtOH mixture. After refluxing for 24 h the dark green solution was concentrated to ~10 mL and on cooling solidified. It was redissolved in CH_2Cl_2, filtered and the filtrate concentrated to dryness to produce **83**. Four ions for tetranuclear combinations (Table 7·6) clearly stand out above the background in the FAB-ms. The peak at 1688 cm^{-1} in the IR is proposed to be for the carbonyl of the acetic acid groups in the formula for this complex.

It is thought that coordinated acetic acid is also found in complex **84**. A portion of **83** was refluxed for 24 h with an excess of $NaClO_4$ and then concentrated to ~10 mL. This was allowed to evaporate to dryness and mixed with 300 mL of water. The green powder which did not dissolve was collected by filtration. In the FAB-ms (Table 7·6) peaks are seen for tetranuclear ions. Evidence for both carbonyl and perchlorate is also seen in the IR. Chemical analysis agrees with the formulation of complex **84** as $[Ni_4(\mu\text{-}OH)\mathbf{LV5t}(CH_3COO)_2(CH_3COOH)_3(ClO_4)]\cdot CH_3CH_2OH$.

Table 7·6 : Selected FAB-ms ions for LV5t - CH_3COO^- complexes

		83	84	85	86	87
LV5t, 4Ni, O, $4N_3$, Cl,	1023·03			1020·3		
LV5t, 4Ni, OH, 2HOAc	941·12	941				
LV5t, 4Ni, NCS, OAc	921·06		921·0			
LV5t, 4Ni, 2NCS	920·03					
LV5t, 4Ni, ClO_4	920·02					
LV5t, 4Ni, OH, HOAc	881·10	881	881·0			
LV5t, 4Ni, O, OH	837·08					
H**LV5t**, 4Ni, OH	822·08	822	822·0	822·0		
H_2**LV5t**, Ni, 2NCS	748·23				748·0	748·0
H_2**LV5t**, 2Ni, NCS	748·19					
H_3**LV5t**, Ni, 3Cl	738·20		740·9			
H_2**LV5t**, 2Ni	690·22				690·1	690·0
H_3**LV5t**, Ni	633·29				632·0	633·0
LV5t, Cl	607·30					605·0

Complex **85** formed when 400 mg of **83** was dissolved in 25 mL of MeOH and excess NaN_3 in hot MeOH added. The mixture was stirred at boiling point for 30 mins and complex **85**, a pale yellowish green powder separated from the green solution. FAB-ms (Table 7·6) and chemical analyses support the assignment of **85** as tetranuclear complexes and it is assigned the formula $[Ni_4(\mu\text{-}OH)\mathbf{LV5t}(N_3)_2Cl_2(CH_3COOH)]\cdot CH_3OH$.

Complexes **86**, **87**, and **88** were sequentially isolated from a synthesis which was initially set up as for complex **83** but at the onset of refluxing a solution of excess NH_4NCS in MeOH was added. Complex **86** was filtered off the dark green solution as a yellow-green powder. No distinctive pattern is visible in the IR. Nickel analysis suggested that this was a binuclear product and so did the FAB-ms (Table 7·6). These indicators along with the chemical analysis supported the formula $[Ni_2(H_4\mathbf{LV5t})Cl_2(NCS)_2]\cdot 1{\cdot}5CH_3CH_2OH$ for complex **86**. Complex **87**, a similar yellow-green powder was isolated from the filtrate of complex **86**. The remaining filtrate was reduced to dryness and water added to it; almost all of the solid remained undissolved and was collected as complex **88**. The IRs of these two products are almost identical. The FAB-ms of **87** (Table 7·6) shows the same ions as found in the spectrum of **86**; no FAB-ms was done of **88**. Chemical analysis supports the formulae $[Ni_2(H_4\mathbf{LV5t})Cl(NCS)_3]\cdot CH_3CH_2OH\cdot CH_3OH$ for complex **87** and $[Ni_2(H_4\mathbf{LV5t})(NCS)_4]\cdot 2{\cdot}5CH_3CH_2OH$ for **88**.

3 : THE PERCHLORATE COMPLEXES

It was hoped that the nickel perchlorate complexes if crystalline would not exhibit disorder to the same extent as the acetate ones had and thus emphasis, in the nickel section of this work, was on the preparation of perchlorate complexes.

3·1 : Perchlorate complexes with LV5

Table 7·7 : Perchlorate complexes of LV5

89	$[Ni_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot 6H_2O\cdot 2CH_3OH$
90	$[Ni_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot [Ni_2Cl_4]\cdot 3CH_3CH_2OH$
91	$[Ni_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot 5H_2O\cdot 2CH_3OH$
92	$[Ni_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot 4CH_3CH_2OH\cdot H_2O$
93	$[Ni_2(H_4\mathbf{LV5})(NCS)_3ClO_4]\cdot H_2O\cdot CH_3CH_2OH$

Of the five complexes made with **LV5** and nickel perchlorate four, are proposed to be tetranuclear and one binuclear. These are shown in Table 7·7. For all of the tetranuclear products a fragment (mass ~ 837) for the core containing four

nickel ions, an oxygen and one associated perchlorate ion is seen in the FAB-ms (Table 7·9). These four complexes also exhibit similar features in their IR spectra (Table 7·8) and show a pattern similar to that seen in the tetranuclear cobalt structures. It is suggested that complex **90** is an polymeric complex with macrocyclic units linked by the Ni_2Cl_4 units.

Table 7·8 : ClO_4 complexes of LV5 with selected IR frequencies (cm^{-1})

89	3415	2925	1645		1553		1100		823	769	723	626
90	3419	2922	1652	1627	1533	1121	1108	1089	836	770	723	626
91	3385	2914	1639		1554		1108	876	823	770	723	626
92	3404	2921	1645		1550		1108		838		724	
93	3412	2923	1647		1540	1122	1109	870	827			

Complex **89** was the second product from a brownish-green reaction mixture which was refluxed for 24 h. The first product (a pale yellow powder) was inorganic. The filtrate was concentrated to ~15 mL and allowed to evaporate slowly. In much the same manner as many previous reactions this resulted in thick oily mass but this time the oil was treated with CH_2Cl_2, dissolved in MeOH and then treated with ether. The resulting yellowish-green powder was collected by vacuum filtration. The tetranuclear nature of this product was supported by chemical analysis agreeing with the assignment of $[Ni_4(\mu_4\text{-OH})$ **LV5**$(ClO_4)_3]\cdot 6H_2O\cdot 2CH_3OH$.

Table 7·9 : Selected FAB-ms ions for LV5 - ClO_4 complexes

		89	**90**	**91**	**92**	**93**
H_4**LV5**, 2Ni, $3ClO_4^-$	904·98				902·7	903
LV5, 4Ni, ClO_4, 2Cl	888·9			889·9		
H_2**LV5**, 2Ni, 3NCS, ClO_4^-	879·00					879
LV5, 4Ni, ClO_4, Cl	853·9			853	854·6	
LV5, 4Ni, O, ClO_4	836·9	836·8	836·8	836·8	836·6	
H_2**LV5**, 2Ni, 2NCS, 3Cl	826·98					827
LV5, 4Ni, 2Cl	794·25			796		
H_4**LV5**, 2Ni, 4Cl, H_2O	769·8	772·9		772·8		769
LV5, 3Ni, 3Cl	771·02					
LV5, 3Ni, O, 2Cl	752·57			753	752·7	
LV5, 4Ni, O,	739·35	737·9	737·8	737·9	737·7	
H_2**LV5**, 2Ni, 2OH, ClO_4	739·43					
H_2**LV5**, 2Ni, ClO_4	707·43	707·0	706·9		706·8	
H_4**LV5**, Ni, ClO_4	649·16			651·8	652·7	
H_2**LV5**, 2Ni,	606·2	606·0	606·0			604
H_4**LV5**, Ni	550·2			549·8		549
H_4**LV5**, $2H_2O$	522·6	520·9	523			
H_4**LV5**	492·62	492·9		492·8	491·7	

The nickel perchlorate reaction, to which TEA had been added, yielded three products all of which appear to be tetranuclear (Tables 7·8 and 7·9). At the end of 24 h refluxing the reaction mixture was a green solution. This was reduced to ~10 mL and kept at room temperature for slow evaporation and once again an oily mass resulted. On treatment of this oil with EtOH a light green powder (complex **90**) formed. The filtrate was set aside and after time another solid had formed. This was collected by filtration and during this process it was noticed that there were two products present; a yellow-green powder (complex **91**) and a lot of bright green crystals (complex **92**) which were separated by hand.

These three complexes have been assigned the formulae **90** $[Ni_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot[Ni_2Cl_4]\cdot 3CH_3CH_2OH$, **91** $[Ni_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot 5H_2O\cdot 2CH_3OH$ and **92** $[Ni_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot 4CH_3CH_2OH\cdot H_2O$. It is speculated that the core, $[Ni_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]$, is conserved in all three structures. Complex **90** is thought to contain Ni_2Cl_4 bridging units similar to the Cu_2Cl_4 seen in a binuclear copper complex of the **LV3** macrocycle.

As with the other metals a nickel perchlorate preparation, in which only two metal equivalents were used, was carried out. The first product from this reaction mixture has not been identified although the FAB-ms supports it being tetranuclear. NaNCS was added to the filtrate and the binuclear complex **93** $[Ni_2(H_4\mathbf{LV5})(NCS)_3ClO_4]\cdot H_2O\cdot CH_3CH_2OH$ was isolated. Complex **93** did not show any distinctive characteristics in the IR but peaks suggesting a binuclear complex could be seen in the FAB-ms. No fragments for a tetranuclear complex were found. Chemical analysis supports the above formula and the 879 ion matches this.

3·2 : Perchlorate complexes with LV5t

Table 7·10 : Perchlorate complexes of LV5t

94	$[Ni_4(\mu\text{-}OH)\mathbf{LV5t}(ClO_4)_4]\cdot 8CH_3CH_2OH$
95	$[Ni_4(\mu_4\text{-}OH)\mathbf{LV5t}(dftp)(ClO_4)_3]\cdot 6H_2O$
96	$[Ni_4(\mu_4\text{-}OH)\mathbf{LV5t}(dftp)(ClO_4)_3]\cdot 4H_2O$

Three products from the syntheses carried out using **LV5t** and nickel perchlorate have been assigned formulae (Table 7·10).

Table 7·11 : Perchlorate complexes of LV5t with selected IR frequencies (cm-1)

94	3421	2960	1653	1624	1108	847			626
95	3405	2955	1642		1108	844	771	730	626
96	3404	2960	1645		1109	845	771	731	

The FAB-ms spectra (Table 7·12) clearly show the formation of tetranuclear macrocyclic complexes.

Table 7·12 : Selected FAB-ms ions for LV5t - ClO_4 complexes

		94	**95**	**96**
LV5t, 4Ni, 2ClO_4, Cl, OH	1057·86			1056·2
LV5t, 4Ni, OH, 2ClO_4, H	1023·42		1025·2	
LV5t, 2Ni, 2ClO_4, 2Cl, OH	973·04		969·1	969·1
LV5t, 4Ni, O, ClO_4, Cl	958·41		953·1	953·1
LV5t, 4Ni, ClO_4, Cl	937·91	938·0		
LV5t, 2Ni, 2OH, 2ClO_4	923·04	921·0		
LV5t, 2Ni, 2ClO_4	889·03		889·2	
LV5t, 2Ni, H_2O, 4Cl	849·96		851·2	856·1
LV5t, 4Ni, OH	823·51	822		
LV5t , 2Ni, 2Cl, 2OH	795·05		791·1	791·1
LV5t , 2Ni, Cl	725·58		725·1	
H_2**LV5t** , 2Ni, OH	709·15		709·1	
H_2**LV5t** , 2Ni	690·13		690·1	690·1
H_3**LV5t**, Ni	633·29		633·1	633·1

The first tetranuclear complex was separated from the reaction mixture which had TEA added. A pale yellow powder (which has not been characterised) was filtered directly from the reaction mixture after 24 h of refluxing and complex **94** was isolated as a deep yellow powder when water was added to the dried filtrate. Compounds **95** and **96** were the second and third products of a standard reaction procedure and also appear to be a tetranuclear folded complexes, similar to the copper complex reported in Chapter 3, and incorporating an extra dftp unit. Most of the peaks seen in the FAB-ms (Table 7·12) are for tetranuclear complexes. The FAB-ms also shows a repeating pattern in the lower mass range indicating that these products are complicated mixtures and contain at least small amounts of other complexes which are probably polymeric in nature.

4 : NITRATE COMPLEXES OF LV5 AND LV5t

Two **LV5** and three **LV5t** complexes (Table 7·13) have been identified from the syntheses in which nickel nitrate was the anion used.

Table 7·13 : Nitrate complexes of LV5 and LV5t

97	$[Ni_4\mathbf{LV5}(NO_3)_4]\cdot CH_3CH_2OH\cdot CH_3OH\cdot 4H_2O$
98	$[Ni_4\mathbf{LV5}Cl_3(NO_3)]\cdot CH_3CH_2OH\cdot 7H_2O$
99	$[Ni_4\mathbf{LV5t}Cl(NO_3)_3]\cdot CH_3CH_2OH\cdot 6H_2O + 3Ni(NO_3)_2$
100	$[Ni_4\mathbf{LV5t}(OH)_2Cl(NO_3)]\cdot[NiCl_4]\cdot 6H_2O$
101	$[Ni_4\mathbf{LV5t}(NCS)_4]\cdot NO_3\cdot HTEA$

Table 7·14 : Nitrate complexes of LV5 and LV5t with selected IR frequencies (cm-1)

97	3380	2914		1769	1641	1551	1383	
98	3414	2916			1639	1553	1384	1354
99	3369	2955		1763	1643	1541	1383	
100	3415	2955		1767	1643	1531	1384	
101	3386	2957	2098		1642	1539	1395	

The **LV5** products came from a reaction mixture to which TEA had been added before the 24 h reflux period. A small amount of unidentified dark green solid was filtered from the dark green reaction mixture. The filtrate evaporated slowly to form a dark green viscous oil and complex **97** was isolated as a light green powder after the addition of EtOH to this oil. This product has been assigned the formula $[Ni_4\mathbf{LV5}(NO_3)_4]\cdot CH_3CH_2OH\cdot CH_3OH\cdot 4H_2O$ on the basis of its chemical analysis. The IR has a look reminiscent of a tetranuclear product but the FAB-ms (Table 7·15) is of little use in confirming this assignment. The dried filtrate of **97** ·had EtOH added and the resulting pale leaf green powder (complex **98**) collected. The FAB-ms (Table 7·15) of this product clearly shows that it is a complex which includes four nickel ions and on the basis of the chemical analysis it has been assigned the formula $[Ni_4\mathbf{LV5}Cl_3(NO_3)]$ $\cdot CH_3CH_2OH\cdot 7H_2O$. It would be expected that Ni_4 complexes would have a μ-OH species in the centre but complexes **97** and **98** do not appear to have this. A possible reason could be that the NO_3 anions are bridging in some manner causing the complex to change from planarity and hinder its inclusion.

Table 7·15 : Selected FAB-ms ions for LV5 - NO_3^- complexes

		97	98
LV5, 4Ni, $6NO_3$	1091·91		1090·9
LV5, 4Ni, $4NO_3$, 3Cl	1072·84		1076·8
LV5, 4Ni, $5NO_3$, Cl	1064·89		1062·8
LV5, 4Ni, O, NO_3	801·35	799·7	799·7
LV5, 2Ni, $2NO_3$, 2Cl	800·88		
H_2**LV5**, Ni, 3Cl, NO_3	799·18		
H_3**LV5**, Ni, $2NO_3$, OH	774·27		774·6
LV5, 2Ni, NO_3	750·19	750	
LV5, Ni, 3Cl	735·18	735·8	737·7
H_4**LV5**, Ni, OH	651·31		653

The $Ni(NO_3)_2$ - **LV5t** synthesis was set up in 70 mL of EtOH and the dahp solution added in a MeOH/EtOH mixture. The dark green reaction mixture was refluxed for 24 h and then concentrated to ~20mL before being left to sit overnight. An unidentified brilliant lime green powder was filtered from the reaction mixture. The dark green filtrate formed a thick oil within 24 h of being set aside. This was treated with ether and formed complex **99** as a lime green solid. The FAB-ms indicates that this is a tetranuclear product and the chemical analysis indicates that it includes either some metal salt or involves some sort of polymeric linking unit involving nickel and nitrate ions. $[Ni_4$**LV5t**$Cl(NO_3)_3]\cdot CH_3CH_2OH\cdot 6H_2O + 3Ni(NO_3)_2$ is speculatively assigned to this.

When TEA was included in the reaction mixture the solution became a brown colour. The brown powder filtered from the reaction mixture after 26 h of refluxing proved to be inorganic. The dark brown filtrate had EtOH added and a precipitate formed immediately. After five days this very fine clay-coloured powder (complex **100**) was collected. The IR of this product gives no clues as to its identity and only two ions (Table 7·16) were clear above the background in the FAB-ms. These are both for tetranuclear fragments. The chemical analysis fits a tetranuclear complex with a Ni_2Cl_4 linking unit; $[Ni_4$**LV5t**$(OH)_2Cl(NO_3)]\cdot[NiCl_4]\cdot 6H_2O$. In reality it is likely that this is a mixture of a tetranuclear and a polymeric product.

Table 7·16 : Selected FAB-ms ions for LV5t - NO_3^- complexes

		99	100	101
LV5t, 4Ni, $5NO_3$, Cl	1152·99	1153·1		
LV5t, 4Ni, $4NO_3$, 2Cl	1121·97	1126·1		
LV5t, 4Ni, $3NO_3$, Cl	1025·00	1027·2		
LV5t, 4Ni, $2NO_3$, Cl	963·02	969·2		
H_2**LV5t**, 2Ni, $2NO_3$,4Cl	954·07			953·2
LV5t, 2Ni, $3NO_3$, Cl	909·14			910·2
LV5t, 4Ni, OH, NO_3, OH_2	901·07 901·03	902·1		
LV5t, 4Ni, NO_3, Cl				
LV5t, 4Ni, OH, 2Cl	891·01			894·2
LV5t, 4Ni, OH, NO_3	883·06		883·9	
LV5t, 4Ni, OH, Cl	856·04	857·1		856·1
LV5t, 2Ni, $2NO_3$, OH	829·18	828·1		
LV5t, 4Ni, OH_2	822·08		823·9	
LV5t, 2Ni, NO_3, OH	767·19	765·1		
H_2**LV5t**, 2Ni, NO_3	752·21			750·1
H_2**LV5t**, 2Ni, 2NCS	748·23			
H_2**LV5t**, 2Ni, Cl	725·19	727·1		
H_2**LV5t**, 2Ni, OH	707·22			706
H_2**LV5t**, 2Ni	690·22	688·1		690·1
LV5t, Cl	607·30	608·1		605·0

A pale cream inorganic powder was the first product collected from a repeat of this synthesis. The filtrate had an excess of NH_4NCS added and was stirred at room temperature for 4 h before being set aside for 11 days. A yellow-brown powder (complex **101**) was filtered from this. It is identified, predominantly on the basis of chemical analysis, as $[Ni_4$**LV5t**$(NCS)_4]\cdot NO_3 \cdot$HTEA. The filtrate of this reaction mixture dried to a deep green oil with a plastic crust. When this was stirred in dry EtOH a solid product which was filtered off became evident. Two components; a yellow-green powder and a blue-green crystalline solid became obvious and were separated by hand. The crystals were investigated by X-ray analysis and their structure is discussed in Chapter 11. The powder has not been identified.

5 : CONCLUSION

The nickel complexes have been by far the hardest to isolate and identify. They appear to be far more soluble than the other metal complexes and this has made it difficult to separate them from the reaction mixtures. A number of

the products were thick oils and treatment of them to produce a solid was not always achieved. Unfortunately the only crystals of macrocyclic nickel complexes were still with acetate ions and were not able to be characterised successfully. Addition of other anions, such as azide, thiocyanate and perchlorate to reaction mixtures have aided in the isolation of products but the more strongly binding anions, especially NCS, often displace the anion under investigation. This is fine if a nickel thiocyanate complex is sought but not helpful if a complex including the anion under investigation is preferred. A better approach may be the addition of bulky but non-coordinating anions to the reaction mixtures.

It is clear that tetranuclear perchlorate complexes have been formed and future work will include finding ways to characterise these.

The acetate syntheses have been the most fruitful but the difficulty of isolating the products has often resulted in other than an acetate structure as discussed above.

Similar problems were encountered in trying to make nitrate complexes.

Chloride complexes are still to be tried.

EXPERIMENTAL - NICKEL COMPLEXES

1 : NICKEL WITH ACETATE

With LV5

Complex 77 : $[Ni_4(\mu\text{-}OH)LV5(CH_3COO)(CH_3COOH)_3]\cdot NiCl_4^{2-}\cdot CH_3CH_2OH\cdot H_2O$

The dahp solution was made by separately dissolving $dahpCl_2$ (2 mmol, 0·382 g) in 15 mL dry EtOH and KOH (4 mmol, 0·224 g) in 15mL dry MeOH. On combining the two solutions KCl precipitated immediately and was removed by filtration as the dahp solution was added to a solution (in 40 mL of dry EtOH) of nickel acetate (4 mmol, 0·995 g) and dfmp (2 mmol, 0·324 g) which had refluxed 10 mins. The bright green solution was refluxed for 24 h and left to cool overnight. After 24 h the volume was reduced by half under vacuum and a minute amount of very fine pale green powder formed. After 2 days the volume was further reduced under vacuum and the product collected.

Yield : 0·330 g, 0·248 mmol, 24·80 %.

IR : 3419, 2909, 1699, 1683, 1661, 1637, 1594, 1505, 1456 cm^{-1}

FAB-ms ($^m/_e$) : 1018·9(3), 992·9(5), 901·7(5), 856·7(12), 796·8(100), 772·7(8), 737·8(44), 679·7(9), 653·7(13), 578·7(7), 549·7(8), 491·7(9), 463·7(7)

Analysis for : $[Ni_4(\mu\text{-}OH)\mathbf{LV5}(CH_3COO)(CH_3COOH)_3]\cdot NiCl_4^{2-}\cdot CH_3CH_2OH\cdot H_2O$

Calculated:	C : 36·69;	H : 4·54;	N : 4·50 %
Found:	C : 36·76	H : 4·59;	N : 4·40 %

A small sample was dissolved in CH_2Cl_2 and set up for ether diffusion. After two recrystallisations and a period of 9 weeks crystals suitable for X-ray were achieved (complex **79**). Although a data set was collected refinement of this structure has not been achieved. Another sample was dissolved in $CHCl_3$ and set up for ether diffusion. Repeated recrystallisations over a period of six months finally yielded crystals suitable for X-ray and again the structure did not refine.

Complex 78 : $[Ni_4(\mu\text{-}OH)LV5(CH_3COO)_3(CH_3COOH)]\cdot CH_3OH\cdot 3H_2O$

$Ni(CH_3COO)_2$ (4 mmol) was dissolved in 20 mL MeOH and added to a solution of dfmp (2 mmol) in 20 mL hot MeOH and the mixture was refluxed for 5 mins. KOH (4 mmol) and dahp (2 mmol) was mixed in 40 mL of dry MeOH. The green reaction mixture was refluxed for 24 h. Green solid started appearing on the walls of the round bottomed flask after 4 h of refluxing. A dark green solid (0·500 g) was filtered from the hot reaction mixture, washed with 3 x 10 mL of MeOH and dried *in vacuo.* This contained visible white crystals (KCl). The green filtrate of was concentrated to ~15 mL and left for 2 h. A green powder (0·360 g) separated and was filtered off and washed with dry MeOH. This also contained some visible white crystals. The filtrate was allowed to dry completely at room temperature, the residue redissolved in CH_2Cl_2, filtered and left to evaporate. 0·150 g of a very light green powder was collected.
The IRs of all these compounds were the same.
A second preparation, done with 8 mmol of $Ni(CH_3COO)_2$ initially yielded 0·530 g of a light green powder which was identified (by IR) as the same as the previous products.
All of these powders were combined and redissolved in CH_2Cl_2 and a very small amount of white solid (probably KCl) was filtered off. The entire filtrate was set up for ether diffusion and a leaf green powder (complex **78**) collected from this.
Overall yield : 1·54 g, 1·445 mmol, 48·17 %.
IR : 3555, 3429, 2916, 2851, 1638, 1593, 1545, 1456, 1406, 1236, 1124 cm^{-1}.
FAB-ms ($^m/_e$) : 855·8(12), 810·7(4), 796·7(100), 737·8(19), 652·7(7), 491·7(5).

Analysis for : $[Ni_4(\mu\text{-}OH)$**LV5**$(CH_3COO)_3(CH_3COOH)]\cdot CH_3OH\cdot 3H_2O$

Calculated :	C : 41·78;	H : 5·31;	N : 5·27 %
Found :	C : 41·89;	H : 5·18;	N : 5·31 %

Complex 80 : $[Ni_2(OH_2)(H_4LV5)(OH)(NCS)_3]\cdot H_2O$

0·3 g of **78** was taken in MeOH, excess NH_4NCS added, and the reaction mixture stirred at room temperature for some hours. The resulting yellow powder was collected by filtering and washed with 3 x 3 mL of MeOH.
Yield : 0·210 g, 0·251 mmol, 89·16 %.
IR : 3384, 2920, 2095,1642,1542, 1452 cm^{-1}

Analysis for : $[Ni_2(OH_2)(H_4\mathbf{LV5})(OH)(NCS)_3]\cdot H_2O$

Calculated:	C : 44·47;	H : 4·94;	N : 11·71 %
Found:	C : 44·64;	H : 4·75;	N : 11·83 %

Complex 81 : $[Ni_2(H_4LV5)Cl_{1.5}(NCS)_{2.5}]\cdot CH_3OH$

0·4 g of **78** was treated by the same procedure as **80**. After stirring a greenish fine powder complex **81** was collected.

Yield : 0·130 g, 0·0701 mmol, 37·37 %.

IR : 3407, 2921, 2093, 1639, 1539, 1456(wk) cm^{-1}

FAB-ms ($^m/_e$) : 816·19(2) - virtually nothing above background.

Analysis : $[Ni_2(H_4\mathbf{LV5})Cl_{1.5}(NCS)_{2.5}]\cdot CH_3OH$

Calculated :	C : 45·17;	H : 4·65;	N : 11·04;	S: 9·72 %
Found :	C : 45·16;	H : 4·76;	N : 10·77;	S; 10·06 %

Complex 82 : $[Ni_2(H_4LV5)Cl(NCS)_3]$

A similarly coloured powder was collected from the filtrate of **82**

Yield : 0·117 g, 0·1432 mmol, 57·05 %.

IR : 3400, 2920, 2872, 2095, 1639, 1541, 14497, 1231, 872, 822, 771 cm^{-1}.

FAB-ms ($^m/_e$) : 919·2(7), 613·1(100). - virtually nothing above background.

Analysis : $[Ni_2(H_4\mathbf{LV5})Cl(NCS)_3]$

Calculated :	C : 45·42;	H : 4·43;	N : 11·96;	S : 11·73 %
Found :	C : 45·49;	H : 4·53;	N : 11·74;	S : 11·52 %

With LV5t

Complex 83 : $[Ni_4(\mu\text{-}OH)LV5tCl_2(CH_3COO)(CH_3COOH)_2]\cdot 2CH_3OH\cdot CH_3CH_2OH$

$Ni(OAc)_2$ (8 mmol) was dissolved in 40 mL MeOH and added to a solution of dftp (4 mmol) in 35 mL hot MeOH and the mixture was refluxed for 5 mins. KOH (8 mmol) and dahp (4 mmol) was mixed in 35 mL of 1 : 1 dry MeOH : EtOH. The resulting dark green solution was refluxed for 24 and concentrated to ~ 10 mL. On cooling it solidified, was dissolved in CH_2Cl_2 and filtered. The filtrate was concentrated to dryness and the complex dried *in vacuo* .

Yield : 2·1 g, 0· 8793 mmol, 87·93 %

IR : 3398, 3261, 2953, 2901, 1688, 1637, 1599, 1556, 1457, 1412 cm^{-1}

FAB-ms ($^m/_e$) : 988(5), 941(7), 881(100), 822(15)
992·04 - **LV5t**, 4Ni, 2Cl, 2OAc
939·10 - **LV5t**, 4Ni, OH, 2OAc
880·09 - **LV5t**, 4Ni, OH, OAc.
821·08 - **LV5t**, 4Ni, OH.

Analysis for : $[Ni_4(\mu\text{-}OH)\mathbf{LV5t}Cl_2(CH_3COO)(CH_3COOH)_2]\cdot 2CH_3OH\cdot CH_3CH_2OH$
Calculated: C : 44·61; H : 5·96; N : 4·73 %
Found: C : 44·71 H : 5·65; N : 4·40 %

Complex 84 : $[Ni_4(\mu\text{-}OH)LV5t(CH_3COO)_2(CH_3COOH)_3(ClO_4)]\cdot CH_3CH_2OH$

A portion of **83** was refluxed IN EtOH with excess $NaClO_4$ for 24 h and then concentrated to 10 mL. It was kept for slow evaporation for some time and when totally dried the reaction mixture was added to 300 mL of water. The green powder which did not dissolve was collected by filtration and washed with 3 x 10 mL of water.

Yield : 0·113 g, 0·0978 mmol, ~80 %.

IR : 3423, 2958, 1685, 1642, 1560, 1419(wide, spl), 1121(spl), 623 cm^{-1}.

FAB-ms ($^m/_e$) : 921·0(16), 881·0(100), 822·0(70), 740·9(26), - but polymeric look.

Analysis for : $[Ni_4(\mu\text{-}OH)\mathbf{LV5t}(CH_3COO)_2(CH_3COOH)_3(ClO_4)]\cdot CH_3CH_2OH$
Calculated : C : 43·56; H : 5·48; N : 4·42 %
Found : C : 43·81; H : 5·34; N : 4·05 %

Complex 85 : $[Ni_4(\mu\text{-}OH)LV5t(N_3)_2Cl_2(CH_3COOH)]\cdot CH_3OH$

400 mg of **85** was dissolved in 25 mL of MeOH and excess NaN_3 dissolved in hot MeOH added. The mixture was stirred at boiling point for 30 mins and then at room temperature overnight. A small amount of pale yellowish-green solid separated from the green solution, was filtered off, and washed with 3 x 2 mL of MeOH.

Yield : 0·060 g, 0·0516 mmol, 5·16 %.

IR : 3404, 2958, 2088, 1643, 1554, 1457, 1410, 1231 cm^{-1}.

FAB-ms ($^m/_e$) : 1020·3(17), 822·0(39), 640·8(32), 534·9(100), 518·9(90).

Analysis for : $[Ni_4(\mu\text{-}OH)\mathbf{LV5t}(N_3)_2Cl_2(CH_3COOH)]\cdot CH_3OH$
Calculated : C : 41·47; H : 4·99; N : 13·07 %
Found : C : 41·53; H : 5·15; N : 12·81 %

Complex 86 : $[Ni_2(H_4LV5t)Cl_2(NCS)_2]\cdot 1\cdot 5CH_3CH_2OH$

$Ni(OAc)_2$ (4 mmol) and dftp (2 mmol) was dissolved in 60 mL hot MeOH and refluxed for 5 mins. KOH (4 mmol) and dahp (2 mmol) was mixed in 20 mL of 1 : 1 dry MeOH : EtOH and the resulting dahp solution added. After mixing, a solution of excess NH_4 NCS was also added. The dark green solution was refluxed for 24 h, concentrated to ~ 15 mL, and left at room temperature for 48 h. A yellow-green powder was filtered off and washed with 3 x 5 mL of MeOH.

Yield : 0·117 g, 0·1262 mmol, 33·64 %.

IR : 3404, 2959, 2092, 1653, 1539, 1457(spl), 1231 cm^{-1}

FAB-ms ($^m/_e$) : 748·0(53), 690·1(100), 632·0(29), 620·0(16), 605·0(43) - polymeric in lower region.

Analysis for : $[Ni_2(H_4\mathbf{LV5t})Cl_2(NCS)_2]\cdot 1\cdot 5CH_3CH_2OH$

Calculated:	C : 49·39;	H : 5·85;	N : 8·86 %
Found:	C : 49·57;	H : 5·85;	N : 8·95 %

Complex 87 : $[Ni_2(H_4LV5t)Cl(NCS)_3]\cdot CH_3CH_2OH\cdot CH_3OH$

Complex **87** was collected, as a yellow-green powder, from the filtrate of **86** after a few days.

Yield : 0·300 g, 0·3138 mmol, 31·38 %.

IR : 3405, 2957, 2093, 1652,1538, 1456, 1231 cm^{-1}

FAB-ms ($^m/_e$) : 748·0(48), 690·0(100), 633·0(26), 605·0(44),

Analysis for : $[Ni_2(H_4\mathbf{LV5t})Cl(NCS)_3]\cdot CH_3CH_2OH\cdot CH_3OH$

Calculated:	C : 48·93;	H : 5·95;	N : 9·98 %
Found:	C : 49·05;	H : 5·60;	N : 9·86 %

Complex 88 : $[Ni_2(H_4LV5t)(NCS)_4]\cdot 2CH_3CH_2OH$

The filtrate of **87** evaporated to dryness at room temperature leaving a dark lime green powder which was treated with 50 mL of H_2O. It did not dissolve, was collected by filtering and washed with 3 x 25 mL of water.

Yield : 0·305 g, 0·3072 mmol, 30·72 %.

IR : 3415, 2957, 2091, 1653 ,1536, 1459, 1231 cm^{-1}

FAB-ms ($^m/_e$) : nothing above background.

Analysis for : $[Ni_2(H_4\mathbf{LV5t})(NCS)_4]\cdot 2CH_3CH_2OH$

Calculated:	C : 49·52;	H : 5·94;	N : 11·00 %
Found:	C : 49·67;	H : 5·87;	N : 10·80 %

2 : NICKEL WITH PERCHLORATE

LV5

Complex 89 : $[Ni_4(\mu_4\text{-}OH)(ClO_4)_3]\cdot 6H_2O\cdot 2CH_3OH$

$Ni(ClO_4)_2$ (4 mmol) was dissolved in 25 mL MeOH and added to a solution of dfmp (2 mmol) in 25 mL hot MeOH and the dirty green mixture was refluxed for 5 mins. KOH (4 mmol) and dahp (2 mmol) was mixed in 30 mL of dry MeOH. The resulting brownish-green solution was refluxed for 24 h. A small amount of white solid (probably KCl) became apparent almost immediately on commencement of refluxing. The reaction mixture was filtered hot and 0·44 g of a pale yellow powder collected. The IR of this showed it to be a mixture of an inorganic perchlorate complex and some KCl (the white portion not soluble in dmf). The dark green filtrate was concentrated to ~ 15 mL and after a few hours more white solid, which was filtered off, appeared. The rest of the filtrate was left in a beaker for slow evaporation and after a week had become a thick oily mass. This oil was treated with CH_2Cl_2, dissolved in MeOH and ether added. The resulting yellowish green powder was collected in a frit.

Yield : 0·975 g, 0·8051 mmol, 80·51 %

IR : 3415, 2925, 1645, 1533, 1100, 881, 823, 769, 723, 626 cm^{-1}

FAB-ms ($^m/_e$) : 836·8(56), 772·9(61), 737·9(56), 707·0(100), 606·0(79), 520·9(57), 492·9(43), 436·9(53)

Analysis for : $[Ni_4(\mu_4\text{-}OH)(ClO_4)_3]\cdot 6H_2O\cdot 2CH_3OH$

Calculated:	C : 29·76;	H : 4·41;	N : 4·58 %
Found:	C : 29·76	H : 4·25;	N : 4·58 %

Complex 90 : $[Ni_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot 2[Ni_2Cl_4]\cdot 5CH_3CH_2OH$

$Ni(ClO_4)_2$ (4 mmol) and dfmp (2 mmol) were dissolved in 50 mL hot dry MeOH and refluxed for 30 mins. KOH (4 mmol) and dahp (2 mmol) was mixed in 25 mL MeOH and the filtered solution added to the reaction mixture. TEA (4 mmol) was added dropwise and the solution was refluxed for 24 h. The

solution, which was brown to start with, became green after refluxing for one hour. As no solid was visible at the end of the refluxing time the solution was concentrated to ~ 10 mL and kept at room temperature for slow evaporation. When EtOH was added to the resulting green oily mass a light green solid formed. This was collected and washed with 3 x 5 mL EtOH. Although the IR and the FAB-ms showed that a macrocyclic product incorporating four nickels was present, no satisfactory identification could be ascertained from the chemical analysis and it is speculated to be as below.

Yield : 0·150 g, 0·120 mmol, 12·00 %.

IR : 3419, 2922, 1652, 1627, 1533, 1121, 1108, 1089, 626 cm^{-1}

FAB-ms ($^{m}/_{e}$) : 836·8(18), 737·8(24), 706·9(20), 606·0(24), 523(26)

Analysis : $[Ni_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot 2[Ni_2Cl_4]\cdot 5CH_3CH_2OH$

Calculated:	C : 28·32;	H : 3·94;	N : 3·48 %
Found:	C : 28·34	H : 3·25;	N : 3·37 %

Complex 91 : $[Ni_4(\mu_4\text{-}OH)LV5(ClO_4)_3]\cdot 5H_2O\cdot 2CH_3OH$

The filtrate of this product was set aside and after 4 weeks the filtrate contained a solid. During filtering it was noticed that this product included bright green crystals (complex **91**) which were separated by hand. The remainder was a yellow green powder (complex **92**)

Yield : 0·080 g, 0·067 mmol, 6·7 %.

IR : 3385, 2914, 2842, 1639, 1554, 1108, 891, 854, 820, 769, 636, 626 cm^{-1}.

FAB-ms ($^{m}/_{e}$) : 889·9(8), 853(20), 836·8(92). 796(22), 772·8(36), 753(33), 737·9(100), 651·8(27), 549·8(21), 492·8(24)

Analysis for : $[Ni_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot 5H_2O\cdot 2CH_3OH$

Calculated :	C : 30·21;	H : 4·31;	N : 4·70 %
Found :	C : 30·11;	H : 4·94;	N : 4·84 %

Complex 92 : $[Ni_4(\mu_4\text{-}OH)LV5(ClO_4)_3]\cdot 4CH_3CH_2OH\ H_2O$

Yield : 0·327 g, 0·2972 mmol, 29·72 %.

IR : 3404, 2921, 1645, 1550, 1108, 876, 823, 770, 723, 637, 626 cm^{-1}.

FAB-ms ($^{m}/_{e}$) : 902·7(10), 854·6(16), 836·6(100), 822·6(17), 752·7(39), 737·7(92), 706·8(29), 652·7(42), 522·7(54), 491·7(55), 463·7(47).

Analysis for : $[Ni_4(\mu_4\text{-}OH)\mathbf{LV5}(ClO_4)_3]\cdot 4CH_3CH_2OH\cdot H_2O$

Calculated :	C : 34·95;	H : 4·81;	N : 4·53 %
Found :	C : 34·82;	H : 4·70;	N : 4·14 %

Complex 93 : $[Ni_2(H_4LV5)(NCS)_3ClO_4]\cdot H_2O\cdot CH_3CH_2OH$

In this reaction only two mmols of the metal salt was used. The dahp solution was added to the dfmp and $Ni(ClO_4)_2$ which were refluxing in 40 mL of 1 : 1 MeOH : EtOH. The solution rapidly became bright green and was refluxed for 25 h. Some very fine powder appeared after 17 h. The mixture was left for slow evaporation at ambient temperature. After ten days the volume had reduced to approximately two-thirds and a 0·084 g of a yellow-green powder was collected by vacuum filtration. Although IR and FAB-ms showed a tetranuclear macrocyclic product was present chemical analysis revealed only a trace of nitrogen. NaNCS was added to the filtrate and after a few days a large amount of brilliant lime green powder was collected and left to air dry in the frit.

Yield : 0·715 g, 0·6738 mmol, 67·38 %.

IR : 3412, 2095, 1647, 1540, 1122, 1109 cm^{-1}

FAB-ms ($^m/_e$) : 903(26), 879(24), 827(38), 769(33), 604(45), 549(100), 523(62).

UV : 355, 430.

Analysis for :$[Ni_2(H_4\mathbf{LV5})(NCS)_3ClO_4]\cdot H_2O\cdot CH_3CH_2OH$

Calculated:	C : 41·12;	H : 4·60;	N : 10·17	S : 9·98 %
Found:	C : 41·19	H : 4·56;	N : 9·78	S : 10·00 %

With LV5t

Complex 94 : $[Ni_4(\mu\text{-}OH)LV5t(ClO_4)_4]\cdot 8CH_3CH_2OH$

$Ni(ClO_4)_2$ (4 mmol) and dftp (2 mmol) were dissolved in 40 mL EtOH and the green mixture was refluxed for 20 mins. KOH (4 mmol) and dahp (1·68 mmol) (n.b. the wrong amount of dahp was used in this reaction) was mixed in 10 mL MeOH and the filtered solution added dropwise to the reaction mixture. 1 mL (a little over 6 mmol) TEA was added dropwise causing a slight colour change. The reaction mixture was refluxed for 26 h and a 0·583 g of a yellow powder was collected by vacuum filtration. This product was not identified. The filtrate had EtOH added and as no change was noticed this was followed by the addition of water. A pale green precipitate formed immediately.

Yield : 0·724 g, 0·486 mmol, 48·60 %.

IR : 3421, 2960, 1653, 1624, 1529, 1109, 847, 626 cm^{-1}.

FAB-ms ($^m/_e$) : 938·0(15), 921·0(28), 822·0(22), 526·0(57), 423·2(100)

Analysis for : $[Ni_4(\mu\text{-OH})\mathbf{LV5t}(ClO_4)_4]\cdot 8CH_3CH_2OH$

Calculated :	C : 37·75;	H : 5·89;	N : 3·52 %
Found :	C : 38·15;	H : 5·76;	N : 3·30 %

Complex 95 : $[Ni_4(\mu_4\text{-OH})LV5t(dftp)(ClO_4)_3]\cdot 6H_2O$

$Ni(ClO_4)_2$ (4 mmol) and dftp (2 mmol) were dissolved in dry EtOH and the green mixture was refluxed for 20 mins. KOH (4 mmol) and dahp (2 mmol) was mixed in MeOH (and sat for 4 days) and the filtered solution added dropwise to the reaction mixture. The reaction mixture was refluxed without stirring for 23 h and a pale yellow powder (0·162 g) was collected by vacuum filtration. IR established that this was inorganic. The filtrate solidified to a bright green crust, water was added and a deep yellow powder collected.

Yield : 0·714 g, 0·51 mmol, 51·00 %.

IR : 3405, 2955, 1643, 1537, 1089, 844, 771, 730, 626 cm^{-1}.

FAB-ms ($^m/_e$) : 1025·2(6), 969·1(7), 953·1(45), 889·2(48), 851·2(21), 791·1(37) 725·1(26), 709·1(27), 690·1(100)(, 633·1(57), 605·1(99). - very polymeric look in the lower range.

Analysis for : $[Ni_4(\mu_4\text{-OH})\mathbf{LV5t}(dftp)(ClO_4)_3]\cdot 6H_2O$

Calculated :	C : 41·35;	H : 5·28;	N : 4·20 %
Found :	C : 41·33;	H : 5·41;	N : 3·62 %

Complex 96 : $[Ni_4(\mu_4\text{-OH})LV5t(dftp)(ClO_4)_3]\cdot 4H_2O$

After 5 days a greenish yellow powder was collected from the filtrate of **1·12a**

Yield : 0·018 g, 0·0128 mmol, 1·28 %.

IR : 3404, 2957, 1647, 1541, 1109(tr), 845, 771, 731, 626 cm^{-1}.

FAB-ms ($^m/_e$) : 1056·2(9), 997·2(8), 969·1(10), 953·1(45), 911·2(11), 895·2(47), 856·1(18), 791·1(29), 690·1(100), 633·1(54), 607·0 (84), - polymeric look in lower range.

Analysis for : $[Ni_4(\mu_4\text{-OH})\mathbf{LV5t}(dftp)(ClO_4)_3]\cdot 4H_2O$

Calculated :	C : 41·90;	H : 5·20;	N : 4·25 %
Found :	C : 42·11;	H : 5·64;	N : 4·31 %

3 : NICKEL WITH NITRATE

With LV5

Complex 97 : $[Ni_4LV5(NO_3)_4]\cdot CH_3CH_2OH\cdot CH_3OH\cdot 4H_2O$

$Ni(NO_3)_2$ (4 mmol) and dfmp (2 mmol) were dissolved in 50 mL hot MeOH and the green mixture was refluxed for 10 mins. KOH (4 mmol) and dahp (2 mmol) was mixed in 25 mL 1 : 1 MeOH : EtOH and the filtered solution added to the reaction mixture. Triethylamine (TEA) (6 mmol) was added dropwise and the solution was refluxed for 24 h. A small amount of green solid which separated from the dark green solution, was filtered off, dissolved in a mixture of DMF : DMSO : MeOH (2 : 2 : 1) and set up for ether diffusion. The dark green filtrate was kept at room temperature for slow evaporation. When EtOH was added to the resulting oily product, a light green solid formed. This was collected, washed with 3 x 5 mL EtOH and dried.

Yield : 0·6 g, 0·519 mmol, 51·90 %.

IR : 3380, 2914, 1769(tiny), 1641, 1551, 1383(2 pks), 878, 823, 770, 623 cm^{-1}.

FAB-ms ($^m/_e$) : 799·7(100), 750(20), 735·8(38) - only a smidgen above background.

Analysis for :$[Ni_4\mathbf{LV5}(NO_3)_4]\cdot CH_3CH_2OH\cdot CH_3OH\cdot 4H_2O$

Calculated:	C : 30·09;	H : 3·98;	N : 8·10 %
Found:	C : 30·12;	H : 4·04;	N : 8·22 %

Complex 98 : $[Ni_4LV5Cl_3(NO_3)]\cdot CH_3CH_2OH\cdot 7H_2O$

The filtrate was set aside for slow evaporation, dried completely and had EtOH added. A pale leaf green powder was collected from this.

Yield : 0·037 g, 0·0347 mmol, 3·47 %.

IR : 3414, 2916, 1639, 1533, 1384, 820 cm^{-1}

FAB-ms ($^m/_e$) : 1090·9(10), 1076·8(15), 1062·8(19), 1050(12), 799·7(81), 774·6(16), 737·7(100), 653(38).

Analysis for : $[Ni_4\mathbf{LV5}Cl_3(NO_3)]\cdot CH_3CH_2OH\cdot 7H_2O$

Calculated :	C : 33·87;	H : 4·93;	N : 6·58 %
Found :	C : 33·95;	H : 5·12;	N : 6·79 %

With LV5t

Complex 99 : $[Ni_4LV5tCl(NO_3)_3]\cdot CH_3CH_2OH\cdot 6H_2O + 3Ni(NO_3)_2$

$Ni(NO_3)_2$ (4 mmol) and dftp (2 mmol) were dissolved in 70 mL EtOH and the green mixture was refluxed for 10 mins. KOH (4 mmol) and dahp (2 mmol) was mixed in 25 mL 1 : 1 MeOH : EtOH and the filtered solution added to the reaction mixture. The dark green solution was refluxed for 24 h, concentrated under vacuum to ~ 20 mL and left at room temperature overnight. 0·012 g of a brilliant lime green powder which has not been identified was separated from the dark green solution and filtered off.

IR : 3393, 2957, 2924, 2862, 1655, 1632, 1537, 1385, 1232, 872, 829, 783, 768, 625 cm^{-1}.

FAB-ms ($^m/_e$) : 857·2(5), 826·2(9), 799·2(5), 763·2(36), 727·2(100), 690·2(98), 605·1(15), 633·2(16).- polymeric look at ~15 % level throughout

The dark green filtrate was kept at room temperature for 24 h and formed an oily mass which was then treated with ether to form a lime green solid (**99**).

Yield : 1·2 g, 0·7261 mmol, 72·61 %.

IR : 3382, 2960, 1763(t), 1645, 1541, 1384(str), 1231, 825, 770, 729 cm^{-1}.

FAB-ms ($^m/_e$) : 1153·1(21), 1126·1(17), 1027·2(40), 969·2(36), 902·1(71), 857·1(54), 828·1(100), 765·1(88), 727·1(59), 688·1(69), 608·1(98), 522·0(99) - this not much above a polymeric looking background.

Analysis for : $[Ni_4\mathbf{LV5t}Cl(NO_3)_3]\cdot CH_3CH_2OH\cdot 6H_2O + 3Ni(NO_3)_2$

Calculated :	C : 24·98;	H : 3·64;	N : 10·52 %
Found :	C : 24·55;	H : 4·00;	N : 10·52 %

Complex 100 : $[Ni_4LV5t(OH)_2Cl(NO_3)]\cdot[NiCl_4]\cdot 6H_2O$

$Ni(NO_3)_2$ (4 mmol) and dftp (2 mmol) were dissolved in 40 mL EtOH and the bright green mixture was refluxed for 30 mins. KOH (4 mmol) and dahp (2 mmol) n.b. the wrong amount of dahp was used in this reaction was mixed in 10 mL MeOH and the filtered solution added dropwise to the reaction mixture. 1 mL (a little over 6 mmol) TEA was added dropwise causing a slight colour change. The reaction mixture was refluxed for 26 h, concentrated under vacuum to ~ 20 mL and left at room temperature until it had dried completely.

EtOH was added and a 0·262 g of brown solid, which IR showed to inorganic, was collected. The dark brown filtrate had EtOH added and a precipitate immediately formed. The mixture was left to sit for 5 days and a yellowish clay coloured very fine powder collected in a Hirsch funnel.

Yield : 0·254 g, 0·1855 mmol, 18·55 %.

IR : 3415, 2955, 1767, 1643, 1531, 1384(spl), 731, 628(v. wide) cm^{-1}.

FAB-ms ($^{m}/_{e}$) : 883·9(30), 823·9(36), 526·0(100) - v. little above background.

Analysis for : $[Ni_4$**LV5t**$(OH)_2Cl(NO_3)]\cdot[NiCl_4]\cdot 6H_2O$

Calculated :	C : 31·26;	H : 4·48;	N : 5·36 %
Found :	C : 31·25;	H : 4·91;	N : 5·19 %

Complex 101 : $[Ni_4$LV5t$(NCS)_4]\cdot NO_3\cdot$HTEA

$Ni(NO_3)_2$ (4 mmol) and dftp (2 mmol) were dissolved in dry EtOH and the dark green mixture was refluxed for 1 h. KOH (4 mmol) and dahp (2 mmol) was mixed in MeOH (and had sat for 5 days) and the filtered solution added dropwise to the reaction mixture. 1 mL (a little over 6 mmol) TEA was added dropwise causing a slight colour change. The reaction mixture was stirred, without refluxing, (this was not intentional) for 23 h. A pale cream powder (0·101 g) was collected by vacuum filtration; this was inorganic. The filtrate had NH_4NCS added and was stirred for 4 h. The mixture was left to sit for 11 days and a yellow-brown powder collected by vacuum filtration.

Yield : 0·394 g, 0·3272 mmol, 32·72 %.

IR : 3386, 2957, 2097, 1642, 1539, 1396(tr. tiny), 842, 770, cm^{-1}.

FAB-ms ($^{m}/_{e}$) : 953·2(6), 910·2(3), 894·2(7), 856·1(13), 750·1(58), 706(8), 690·1(100), 605·0(33), - polymeric looking in the lower region.

Analysis for : $[Ni_4$**LV5t**$(NCS)_4]\cdot NO_3\cdot$HTEA

Calculated :	C : 43·86;	H : 5·10;	N : 11·63;	S :10·64 %
Found :	C : 43·67;	H : 5·40;	N : 11·75;	S : ~11 %

$[Ni(NCS)_4^{2-}][(CH_3)_3NH^{+}]_2$

The filtrate of complex **101** dried to a deep green oil with a plastic crust. This was stirred with dry EtOH and yielded a yellow-green powder and blue green crystalline solids which were separated by hand.

IR(powder) : 3412, 3152, 3036, 2928, 2866, 2093, 1767, 1652, 1634(sh), 1537, 1387, 1230, 878, 833, 779, 714 cm^{-1}.

IR(crystals) : 3117, 3021, 2983, 2876, 2735, 2511, 2083, 1472, 1384, 1248, 1048, 976.

The crystals were investigated by X-ray crystal structure analysis and had the structure $[Ni(NCS)_4]^{2-}[(CH_3)_3NH^+]_2$ which is discussed in Chapter 11.

Analysis for : $[Ni(NCS)_4]^{2-}[(CH_3)_3NH^+]_2 \cdot 1 \cdot 5H_2O$

Calculated :	C : 27·40;	H : 5·29;	N : 19·17 %
Found :	C : 27·38;	H : 5·29;	N : 19·14 %

CHAPTER 8

THE ZINC COMPLEXES

1 : INTRODUCTION

Zinc is extremely important biologically and after iron, magnesium, sodium and calcium is the most abundant ion in biological systems. A remarkable number of zinc containing hydrolytic enzymes have been characterised and its involvement in the zinc fingers is one of its most interesting roles. The zinc fingers are structural domains in peptides. Near the amino-terminal they contain tandem sequences (nine in the one shown in Fig. 8·1), the invariant ones of which are two cysteine and two histidine residues which are bound to the zinc in the tetrahedral arrangement shown in Figure 8·1. It is thought that the zinc binding might regulate nucleic-acid binding and hence gene expression.

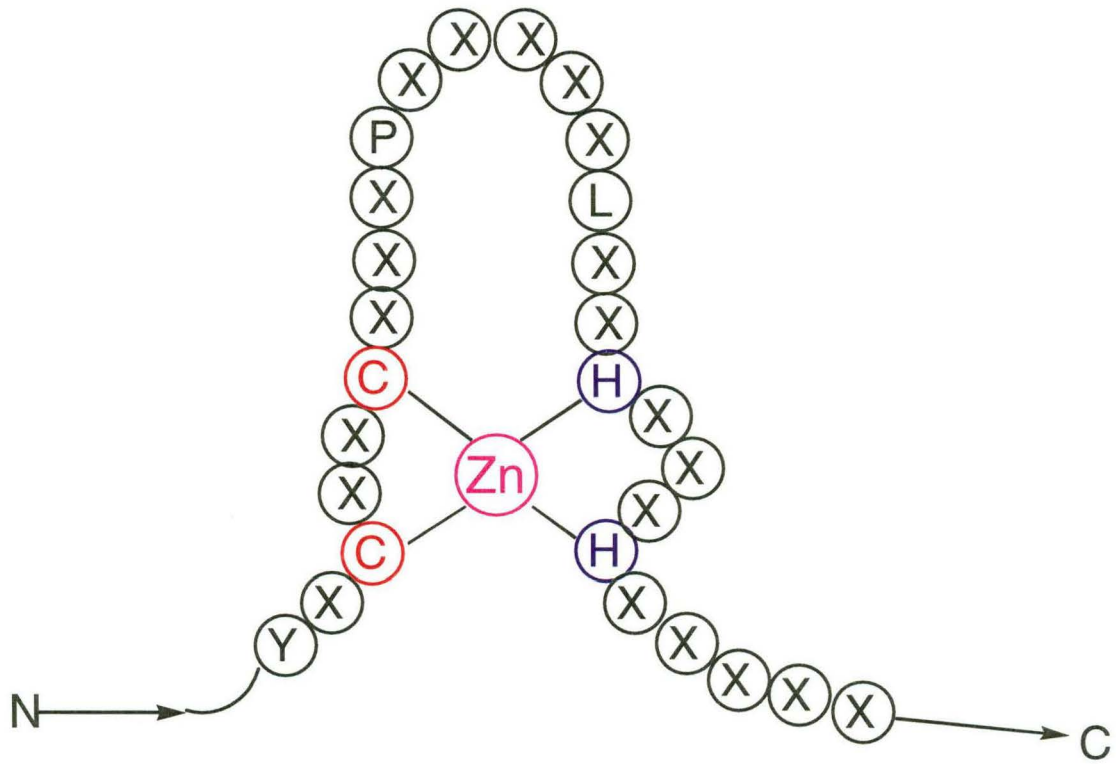


Figure 8·1 : Schematic representation of a zinc finger.[234]
(H = histidine, C = cysteine, P = Phenylalanine, L = Lysine, X = other amino acid residues)

Carboxypeptidase, alkaline phosphatase, alcohol dehydrogenase, and carbonic anhydrase are all examples of hydrolytic zinc enzymes. In carboxypeptidase the Zn(II) is pentacoordinate with the metal ion binding to two imidazole groups from histidine, a bidentate carboxylate from glutamate and a water molecule. Carbonic anhydrase, the first zinc containing enzyme to be discovered, is a lyase which hydrogenates carbon dioxide. The zinc ion is bound tetrahedrally to three histidine residues and a water or hydroxide ion. Hydrolytic processes may be promoted by the **LV5** ligand system.

Like the other Group 12 elements, many of the properties of zinc are related to the fact that it cannot lose any electrons from its filled d shell. It does not form compounds in which the *d*-shell is other than full and there is no evidence for oxidation states higher than II; representing a loss of the outer s electrons. The Zn^{2+} ion is not redox active. Like the *d*-block elements zinc forms complexes with NH_3, amines, halides and cyanide. Cotton[232b] notes however that even with CN^- it is possible that the $d\pi$ bonding between the metal and the ligand is very much lowered compared to the *d*-transition elements, owing to the electronic structure. Zinc forms covalently bound compounds (e.g. $Zn(CH_3)_2$). The polarizing ability of the M^{2+} ion is larger than that predicted by comparing with the radii of the Mg - Ra group and this is because of the greater ease of distortion of the filled *d*-shell.

The aqueous speciation of zinc is well documented with $[Zn(H_2O)_6]^{2+}$, $[ZnCl(H_2O)_5]^+$, $[ZnCl_4]^{2-}$, $[ZnCl_4(H_2O)_2]^{2-}$, and $ZnCl_2(H_2O)_4$ being the most common. Zinc chlorides are anionic. A Cambridge data base search showed that many of these species and $[Zn_2Cl_6]^{2-}$ were often formed as associated moieties when large zinc complexes were synthesised and it is considered by the author that this has been the case in the formation of complexes of **LV5** and **LV5t**.

There is no ligand field stabilisation effect in zinc because of the complete *d*-shells and so stereochemistry is likely to be determined by size, electrostatic forces and covalent bonding forces. The most characteristic stereochemistry of divalent zinc is tetrahedral. In complexes coordination numbers of 4, 5 and 6

are usual but investigations* have shown 5 is more common for zinc than other transition metals.

All of the zinc reaction mixtures, prepared in this project, were refluxed for ~24 h and the products collected as bright yellow or orange-yellow powders. The origin of the colour is the macrocyclic ligand which forms a brilliant yellow fluorescent solution in MeOH or EtOH. In contrast to the cobalt reactions, fewer of the products appear complicated mixtures. No crystals were obtained from either the reaction solutions or from repeated recrystallisation attempts under a variety of conditions. Many of the products were only sparingly soluble in most solvents and therefore even if crystals had been obtained one would have had to be very careful to ensure that these were representative of the bulk sample. The insolubility of these products also meant that it was difficult to obtain good mass spectra of them as not enough sample could reliably be added to the FAB probe tip. This lack of solubility led to experimenting with using the solid samples directly to obtain mass spectra. Usually a sample is dissolved in a suitable solvent and then ~ 10 μL of this solution is added from a syringe to a drop of NOBA matrix which has been applied to the FAB-probe target. This mixture has the solvent removed under vacuum and is then admitted to the mass spectrometer. For the solid samples ~ 5 mg was ground very carefully, using a mortar and pestle, the resulting very fine powder was mixed with the NOBA matrix and ~10 μL of the resulting paste applied to the FAB gun target. Mass spectral data were then obtained as per normal FAB aquisition as previously described (Chapter 2). The results were very good and instrumental in identifying many of the complexes.

* See for example Nelson's study[235]

2 : THE PERCHLORATE COMPLEXES

2·1 : Perchlorate Complexes with LV5

Table 8·1 : Perchlorate complexes of LV5

102	$[Zn_2(H_4\mathbf{LV5})Cl_2OH(ClO_4)]\cdot CH_3OH$
103	$[Zn_2(H_4\mathbf{LV5})(ClO_4)Cl_3]\cdot H_2O$
104	$[Zn_2(H_4\mathbf{LV5})(OH)(ClO_4)(CH_3OH)_2]\cdot[Zn_2Cl_6]^{2-}\cdot 3H_2O$
105	$[Zn_2(H_4\mathbf{LV5})(ClO_4)_3Cl]\cdot 4CH_3OH$
106	$[Zn_2(H_4\mathbf{Lo\text{-}s})(Cl_2)(ClO_4)_2]$
107	$[Zn_2(H_4\mathbf{LV5})(ClO_4)Cl_3]\cdot 2H_2O$
108	$[Zn_4\mathbf{LV5}(ClO_4)_4]\cdot 4CH_3CH_2OH$
109	$[Zn_4\mathbf{LV5}Cl_2(ClO_4)_2]\cdot CH_3CH_2OH\cdot CH_3OH\cdot 5H_2O$

From Table 8·1 it can be seen that six of the complexes formed from reactions between **LV5** and zinc perchlorate have been identified as being binuclear and two as being tetranuclear. Examination of the infrared spectra of all these complexes showed that the first six have the distinctive "binuclear" pattern first identified in the cobalt complexes. These peaks (Table 8·2) are seen at ~870, ~817 and ~ 775 cm^{-1}. Based on these features of the IR it would seem likely that these complexes are similar to the cobalt diagonal binuclear structures. In all of these complexes the imine peak is split. One complex, **106**, is thought to be of the open-sided ligand. Complexes **108** and **109** have patterns in their IR spectra reminiscent of those seen for tetracobalt complexes.

Table 8·2 : Perchlorate complexes of LV5 with selected IR (cm^{-1})

102	3445		2922	1661	1652		1544		1095	871	816	~770			624
103	3440		2927		1653	1635	1545	1108		872	817	~770			625
104	3447		2927	1663		1635	1545		1090	871	817	~770			625
105	3446		2925	1662		1637	1545		1088	870	817	777			625
106	3462	3159	2928		1659	1637	1537		1094	885	816	775			626
107	3449		2926		1658	1641	1537	1109		885	815	775			626
108	3338		2918		1659		1537	1150 1121	1095	885	816	775	722	641	627
109	3450	3227	2926		1655	1634	1543	1170	1092	870	813	775	719		621

The first of these complexes was a deep yellow powder isolated from a reaction which had been refluxed for 20 h. This powder was stirred in boiling CH_3CN and the undissolved material collected by filtering. This residue was identified as **102** $[Zn_2(H_4\mathbf{LV5})Cl_2(OH)(ClO_4]\cdot CH_3OH$. Most of the filtrate was used in a variety of unsuccessful recrystallisation attempts. One aliquot was set aside for

slow evaporation and eventually dried to yellowy-brown shiny flakes. These were shown by IR, FAB-ms and analysis, to be the same as **102**.

Two products were obtained when the synthesis was repeated; a mid-yellow powder was recovered directly from the reaction mixture and a bright yellow powder later formed on the walls of the flask in which the filtrate was left standing. Again they are clearly binuclear products with the first being an homogenous mixture of a binuclear macrocyclic complex with some unidentified material, whereas the second is assigned the formula **103** $[Zn_2(H_4\mathbf{LV5})(ClO_4)Cl_3]\cdot H_2O$.

The third time the synthesis was tried a tiny amount of microcrystalline yellow crust (which has not been identified) formed around the solvent line of the reaction mixture and after a further two weeks a brownish-yellow powder **104** $[Zn_2(H_4\mathbf{LV5})(OH)(ClO_4)(CH_3OH)_2]\cdot[Zn_2Cl_6]^{2-}\cdot 3H_2O$ was collected from the filtered solution. The chemical analysis of **104** agrees with it containing $Zn_2Cl_6^{2-}$ as well as the binuclear macrocyclic compound and this moiety has occurred in a number of syntheses where one of the starting materials is $ZnCl_2$. One example is **M23**$\cdot[18\text{-crown-6-ZnCl}\cdot H_2O]^{+}{}_2\cdot[Zn_2Cl_6]^{2-}$ (Fig. 8·2) which formed when a solution of zinc chloride in ether was allowed to diffuse into a solution of 18-crown-6 in 1,2-dichloroethane.[236] Interestingly, when **M23** was recrystallised from a 2 : 1 CCl_4/acetone mixture an extensively hydrolysed material of the composition **M23**$\cdot[Zn(H_2O)_6]^{2+}[ZnCl_3(H_2O)]^{-}\cdot 2[(18\text{-crown-6})\cdot(CH_3)_2CO]$ was formed. It is not unlikely that species such as $[Zn(H_2O)_6]^{2+}$ and $[ZnCl_3(H_2O)]^{-}$ could be formed during the synthesis of zinc complexes of **LV5** and **LV5t**. The crystal structure of **M23** revealed it to have an extensive three dimensional hydrogen-bonded network between the macrocyclic unit and the zinc species.

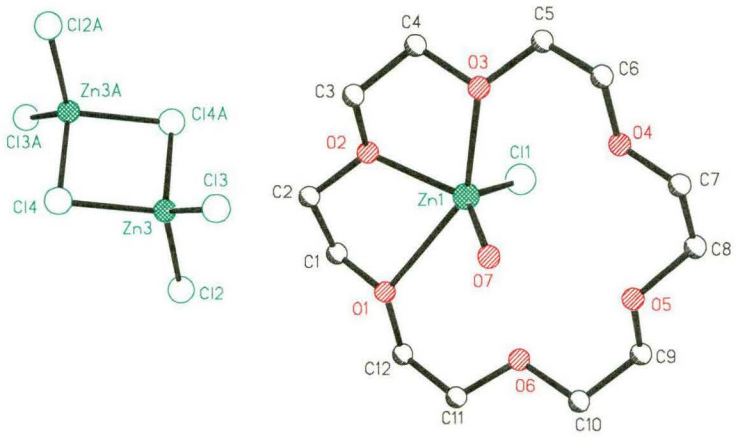


Figure 8·2 : $[18\text{-crown-6-ZnCl}\cdot H_2O]^{+}_2\cdot[Zn_2Cl_6]^{2-}$ showing only one of the crown ether moieties

When this synthesis was carried out with just two metal equivalents a total of four products were isolated and identified and differences were noted in the way that the reaction proceeded. As the first solid started appearing around the solvent line of the reaction mixture within 2 h of the reaction beginning, the reflux time was shortened to 17 h and then the mixture left to cool overnight. This yellow powder was collected under vacuum and is proposed to be **105** $[Zn_2(H_4\mathbf{LV5})(ClO_4)_3Cl]\cdot 4CH_3OH$. When the dehydrated filtrate of **105** had ethanol added to it very little dissolved and two compounds were collected when this mixture was filtered. These were a bright yellow powder and some orange crystalline material. The powder is identified as complex **106** $[Zn_2(H_2\mathbf{Lo\text{-}s})Cl_2)(ClO_4)_2]$; this assignment being based on the peaks seen in the FAB-ms (Table 8·3) and the chemical analysis. The crystalline product as is formulated as complex **107** $[Zn_2(H_4\mathbf{LV5})(ClO_4)Cl_3]\cdot 2H_2O$. Unfortunately these crystals were not good enough for X-ray structure analysis. The filtrate was again dried and EtOH added and this time a very fine yellow powder, complex **108**, remained undissolved. The IR of this material indicates that it is tetranuclear and chemical analysis agrees with the formulation $[Zn_4\mathbf{LV5}Cl_2(ClO_4)_2]\cdot CH_3CH_2OH\cdot CH_3OH\cdot 5H_2O$.

A further repeat of the **LV5** - zinc perchlorate preparation produced a different compound. The reaction mixture was refluxed for 24 h and the dark yellow powder filtered from the hot mixture. It had a tetranuclear pattern in its IR and has been assigned the formula **109** $[Zn_4\mathbf{LV5}(ClO_4)_4]\cdot CH_3CH_2OH\ CH_3OH\cdot 4H_2O$.

Table 8·3 : Selected FAB-ms ion for LV5 - ClO_4 Complexes

		102	103	104	105	106	107	108	109
H **LV5**, 2Zn, 2Cl, $2ClO_4$	884·9								884·9
LV5, 4Zn, 4Cl, H	884·8								
H_2 **LV5**, 2Zn, 3Cl, ClO_4	822·0	823·1							
H_2 **LV5**, 2Zn, $2ClO_4$	816·0	819			819·0				
H_2 **LV5**, 2Zn, 2Cl, ClO_4	787·1						787·3		784·9
H_2 **LV5**, 2Zn, ClO_4	717·1	719·1	719·1	719·0	719·0		719·1	721	719·0
H_2 **LV5**, Zn, ClO_4	653·1	653·0			655·0		655	657	657
H_2**LV5**, 2Zn, Cl									
H_2**Lo-s**, 2Zn, ClO_4	635·9					636·9			
H_3 **LV5**, 2Zn, H	619·1	619·1	619·1	619·0	619·0				619·1
H_2**Lo-s**, Zn, ClO_4	572·1		573·1			573·0	573·0		
H_3 **LV5**	555·2	555·2	555·2	555·1	555·1				555·2
H_2**Lo-s**, 2Zn, H_2O, H	554·0						554·8	554·8	
H_4**LV5**	493·3	493·2	493·2	493·2	493·2		493		
H_2**Lo-s**	473·1		473·1	473·1	473·0	473·1	473·0	472·9	

Syntheses carried out in the presence of TEA produced materials that appear to be polymeric and have not been identified. The FAB-ms of these products show that there are tiny amounts of macrocyclic compounds present.

2·2 : Perchlorate Complexes with LV5t

Table 8·4 : Perchlorate complexes of LV5t

110	$[Zn_4$**LV5t**$(ClO_4)_4]\cdot 8H_2O$
111	$[Zn_4$**LV5t**$(ClO_4)_4]\cdot 0{\cdot}5CH_3CN\cdot H_2O$
112	$[Zn_4$**LV5t**$(ClO_4)_4]\cdot CH_3CH_2OH$
113	$[Zn_4$**LV5t**$(OH)(ClO_4)_3]\cdot TEA\cdot CH_3CH_2OH$

The preparations carried out with the **LV5t** ligand have resulted in the formation of a number of tetranuclear and polymeric complexes only four of which have been assigned formulae (Table 8·4). Features in the IR of all these complexes support the formation of tetranuclear compounds (Table 8·5). This is in contrast to the **LV5** ligand where binuclear complexes dominated. The first of these is identified as **110** $[Zn_4$**LV5t**$(ClO_4)_4]\cdot 8H_2O$. The FAB-ms of **110** (Table 8·6) is dominated by ions for the full macrocycle incorporating four zincs, but in the lower mass range there is a distinctive repeating pattern indicative of some other material probably of a polymeric nature. No speculative complex can be made to very closely match the analysis also suggesting that more than one product has been formed. The closest is for $[Zn_4$**LV5t**$(ClO_4)_4]\cdot 8H_2O$.

Table 8·5 : Perchlorate complexes of LV5t with selected IR (cm^{-1})

110	3449	3217	2960	1659	1541	1120	1089	941	892	841	774	626	
111	3446		2925	1653	1559	1142	1122	1096	899	875	816	770	625
112	3441		2918	1651	1543	1122	1109	1087	984	874	810	772	
113	3439		2960	1652	1549	1140	1121	1093	977	899	832	774	

When the synthesis was repeated, the reaction mixture was taken to dryness under vacuum and CH_3CN added. As the entire preparation redissolved it was set aside in a stoppered flask for quite some time. Eventually complex **111** $[Zn_4$**LV5t**$(ClO_4)_4]$ was collected as a lemon powder. The filtrate was allowed to dry and had water added. The undissolved bright yellow powder, complex **112**, was collected by vacuum filtration and it has been assigned the formula $[Zn_4$**LV5t**$(ClO_4)_4]\cdot CH_3CH_2OH$. These assignments are based on mass spectral data (Table 8·6) and the chemical analyses.

Table 8·6 : Selected FAB-ms ions for LV5t - ClO_4 complexes

		110	**111**	**112**	**113**
LV5t, 4Zn, $2ClO_4$, 2OH	1059·9				1057·6
LV5t, 4Zn, 4Cl	967·9	966·5			
LV5t, 4Zn, ClO_4, H_2O	945·0	945			946·6
LV5t, 4Zn, 3Cl	932·9		931·7		
LV5t, 3Zn, TEA, H_2O	884·3				884·6
LV5t, 3Zn, TEA	866·3				866·0
LV5t, 4Zn, Cl	863·0	866·6	865·7	864·6	
LV5t, 3Zn, Cl	799·1	802·7	800·1	801	802·7

When the preparation was carried out in the presence of TEA a tetranuclear complex was isolated. The lemon-yellow microcrystalline material coated the walls of the reaction flask when it had been left to cool overnight after the reaction mixture had refluxed for 24 h. This complex has been identified as **113** $[Zn_4$**LV5t**$(OH)(ClO_4)_3]\cdot TEA\cdot CH_3CH_2OH$.

3 : THE NITRATE COMPLEXES

Table 8·7 : Nitrate Complexes of LV5 and LV5t

2·1a	$[Zn_4$**LV5**$(NO_3)_2Cl_2]\cdot 4H_2O$
2·1b	$[Zn_4$**LV5**$(NO_3)_2Cl_2]\cdot 2CH_3OH\cdot 2H_2O$
2·2a	$[Zn_4$**LV5t**$(NO_3)Cl_3]\cdot HTEA^+Cl^-$

Table 8·8 : Nitrate Complexes of LV5 and LV5t with selected IR (cm^{-1})

2·1a	3429	2916	1647		1556	1384	1322	890			813	772	693
2·1b	3421	2918	1652		1557	1384	1327	893			813	770	
2·2a	3447	2953	1645	1624	1553	1384		883	859	835	816	774	

Both the syntheses tried with **LV5** and **LV5t** and zinc nitrate were carried out in the presence of TEA. In the **LV5** reaction a turbidity was noticed in the reaction mixture as soon as the TEA was added. A pale yellow powder formed during the 24 h reflux period and was collected by vacuum filtration. Features in the IR show this to be a tetranuclear complex and from the analysis it is identified as **114** $[Zn_4\mathbf{LV5}(NO_3)_2Cl_2]\cdot 4H_2O$. In the FAB-ms peaks are seen for ions of a greater mass then the proposed complex which may indicate that the macrocyclic units are linked by zinc complexes of some sort. The nitrate peak in the IR of complex **114** is very complicated and this appears to support this speculation. This reaction mixture yielded a second product, complex **115**, which from chemical analysis is $[Zn_4\mathbf{LV5}(NO_3)_2Cl_2]\cdot 2CH_3OH\cdot 2H_2O$. This is supported by the FAB-ms and the IR.

Table 8·9 : Selected FAB-ms ions for complexes 2·1a and 2·1b

		114	**115**
LV5, 4Zn, $6NO_3$,	1115·9	1115·8	
LV5, 4Zn, $5NO_3$, Cl	1088·9	1089·0	
LV5, 4Zn, $4NO_3$, Cl	1026·9	1024	
LV5, 4Zn, $3NO_3$, 2Cl	999·9	999·0	
H**LV5**, 4Zn, $2NO_3$, 3Cl	972·8	973	
LV5, 4Zn, $2NO_3$, Cl, H_2O	920·9		920·9
LV5, 4Zn, 3Cl, OH	865·9	863·9	
LV5, 4Zn, NO_3, H_2O,	823·9	825·9	825·9
LV5, 4Zn, Cl, H_2O	796·9	798·9	798·9

The **LV5t** reaction produced complex **116** which is assigned the formula $[Zn_4\mathbf{LV5t})(NO_3)Cl_3]\cdot HTEA^+Cl^-$ (Table 8·7). The IR (Table 8·8) is quite different to the previous ones and shows neither a pattern for a binuclear complex or a tetranuclear one. The nitrate peak in the IR is very small indicating that not much is present and the CH_3 area is quite complex which tends to support the inclusion of TEA in the structure. The FAB-ms (Table 8·10) supports the formation of a tetranuclear complex but otherwise is not very informative.

Table 8·10 : Selected FAB-ms for Complex 2·2a

		116
LV5t, 4Zn, $4NO_3$, Cl, TEA, H_2O	1196·1	1197·9
LV5t, 4Zn, O, 2Cl	913·9	911·9
LV5t, 4Zn, H_2O	846·1	848·9
LV5t, 3Zn, 2Cl	834·1	832·9
LV5t, 4Zn	828·1	
LV5t, Zn, NO_3	698·2	698·9
Lo-st, 2Zn, NO_3, OH	698·1	
H_2**Lo-st**, Zn, NO_3	683·1	683
H_4**Lo-st**, Zn, H	559·2	559·0

4 : THE CHLORIDE COMPLEXES

4·1 : Chloride Complexes with LV5

Table 8·11 : Chloride Complexes of LV5

117	$[Zn_3$ **LV5**$Cl_3]\cdot H_2O\cdot 2CH_3OH$
118	$[Zn_4$**LV5**$(OH)_2Cl_2]\cdot H_2O$

Table 8·12 : Chloride Complexes of LV5 with selected IR (cm^{-1})

117	3447	2924	1653	1635	1545		870	817	776
118	3439	2915	1651		1555	968	887	813	771

The first reaction in the **LV5** with zinc chloride series was set up in the usual manner but only the first half of the dahp solution had been added through a filter paper at the top of the condenser when the procedure was interrupted. By the time, over an hour later, it was possible to add the rest of this solution a significant amount of bright yellow powder, complex **117**, was already visible in the reaction mixture. A trinuclear complex can be made to fit the data for complex **117**. Chemical analysis closely fits the formulation $[Zn_3$**LV5**$Cl_3]\cdot H_2O\cdot 2CH_3OH$. Few ions are seen in the FAB mass spectrum and the parent is for a trinuclear product. In spite of this, it is not thought that the **LV5** ligand system forms trinuclear complexes even though Robson has reported a trinuclear cobalt complex of his **LAmP$_r$** ligand. The IR of **117** has the usual binuclear pattern and it is more likely that it is a binuclear complex and some sort of zinc anion.

Table 8·13 : Selected FAB-ms ions for LV5 - Chloride complexes

		117	118
LV5, 4Zn, O, Cl	801·7		800·8
H**LV5**, 3Zn, H	681	683	
H_2**LV5**, 2Zn, Cl	653·1	655	
H_2**Lo-s**, 2Zn, Cl	573·1		
H_3**LV5**, Zn	555·2	555·1	
H_2**Lo-s**, Zn	473·1		

When the synthesis was carried out in the presence of TEA a turbidity was noticed in the reaction mixture as soon as the TEA was added. Complex **118** was collected as a pale yellow powder from the filtered reaction mixture. From features in the IR and the chemical analysis complex **118** is proposed to be $[Zn_4$**LV5**$(OH)_2Cl_2]\cdot H_2O$.

4·2 : Chloride Complexes with LV5t

Table 8·14 : Chloride Complexes of LV5t

119	$[Zn_4$**LV5t**$Cl_4]\cdot 4CH_3CH_2OH$
120	$[Zn_4$**LV5t**$(dftp)_2(NCS)_2Cl_2]\cdot NH_4^+NCS^-\cdot NH_4^+Cl^-$
121	$[Zn_4$**LV5t**$Cl_4]\cdot 2CH_3CH_2OH$
122	$[Zn_4$ **LV5t**$Cl_4(dftp)_2]\cdot 4H_2O$

The initial products from reactions between **LV5t** and zinc chloride were tetranuclear with or without the presence of TEA in the reaction mixture.
In the reaction from which **119** $[Zn_4$**LV5t**$(OH)Cl_3]\cdot 3CH_3CH_2OH$ was isolated, a reddish oily material formed on the walls of the reaction flask and a yellow solid on the bottom. The mother liquor was decanted off and the solid collected and dried. The complex was identified by IR, FAB-ms and analysis. NH_4NCS was added to the filtrate of **119** and after two weeks a yellow powder, complex **120**, collected.

Table 8·15 : Chloride Complexes of LV5t with selected IR (cm^{-1})

119	3439	2956		1657	1635		1542	958	885	840	776
120	3433	2960	2077	1655		1581	1556	980	891	831	775
121	3441	2956		1648			1551	973	895	832	775
122	3439	2960		1646			1548			841	775-760	726

The IR of this product indicates that it is a tetranuclear complex and this is supported by the peaks for tetranuclear fragments seen in the FAB-ms. The assignment of **120** as a folded complex with bound dftp fragments and the inclusion of ammonium salts is purely speculative but fits the chemical analysis well. A 50 : 50 mix of a binuclear and a tetranuclear complex ($0{\cdot}5[Zn_2(H_4\mathbf{LV5t})(NCS)_3Cl]$ & $0{\cdot}5[Zn_4(\mathbf{LV5t})(NCS)Cl_3]$) fits the chemical analysis equally well but is not supported by either the IR or the FAB-ms.

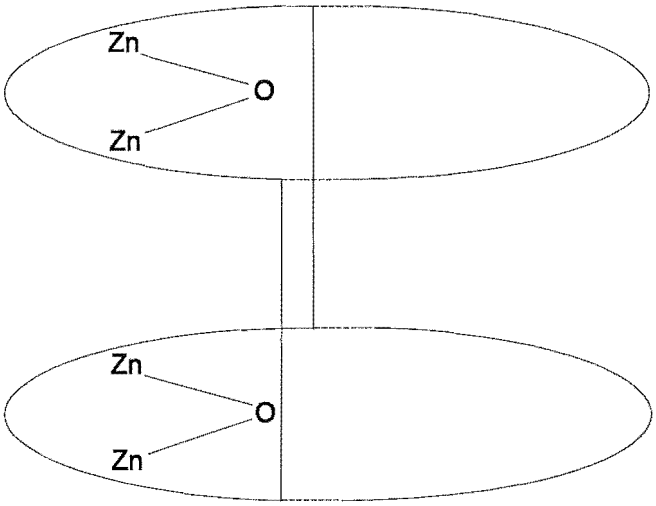


Figure 8·3 : Proposed structure for the folded zinc macrocycle

Table 8·16 : Selected FAB-ms ions for LV5t - chloride complexes

		119	120	121	122
LV5t , 4Zn, 4Cl, Zn_2Cl_3	1200·7		1198·1		
LV5t , 4Zn, 4Cl, 4NCS	1199·8				
LV5t , 4Zn, 4Cl, $ZnCl_2$	1101·7		1103·0		
LV5t , 4Zn, 3Cl, 3NCS	1106·9				
LV5t , 4Zn, 7Cl	1072·8		1070·0		
LV5t , 4Zn, 2Cl, 3NCS	1071·9				
LV5t , 4Zn, 4Cl	967·9		969·0		975
LV5t , 4Zn, Cl, H_2O	881·0		885·0	885·0	883·0
H_2**LV5t** , 2Zn	702·2	703	701·0		
H_2**Lo-st**, 2Zn, Cl,	657·1			657·1	657·1
H_3**LV5t**, Zn, OH	657·2				
H_2**Lo-st**, Zn	557·1				557·1
H_2**Lo-st**, OH	510·1			508·1	510·0

When TEA was included in a reaction mixture, a tetranuclear complex, **121** $[Zn_4$**LV5t**$Cl_4]\cdot 2CH_3CH_2OH$ was collected as a yellow powder.

The dried filtrate of **121** was treated with EtOH and the undissolved material collected. Again, a folded complex **122** $[Zn_4$ **LV5t**$Cl_4(dftp)_2]\cdot 4H_2O$ has assigned to the second reaction product.

5 : THE ACETATE COMPLEXES

Table 8·17 : Acetate complexes of LV5t

123	$[Zn_2(H_2$**LV5t**$)(NCS)_4]\cdot 2CH_3CH_2OH$
124	$[Zn_2(H_4$**LV5t**$)(NCS)_4]\cdot NH_4NCS\cdot 3CH_3CH_2OH$

No acetate reactions with **LV5** were tried and the synthesis with **LV5t** had NH_4NCS added to the reaction mixture after the dahp had been added. A "fluffy" yellow precipitate formed almost immediately. The mixture was refluxed for 24 h after which time an orange solid, complex **123**, was filtered from the hot mixture. A yellow powder, **124**, was collected from the filtrate after it had been left standing at RT.

Table 8·18 : Acetate complexes of LV5t with selected IR (cm^{-1})

123	3433	2953	2085	1662	1637	1527	976	955	887	681
124	3433	2953	2077	1663	1637	1527	976	955	887	681

The IR of the second product appears to be exactly the same as the first; both of these are dominated by a NCS peak and there is no evidence of acetate being present.

Table 8·19 : Selected FAB-ms ion for LV5t - Acetate complexes

		123	124
LV5t, 2Zn, NCS, 2Cl	828·1	828·3	
LV5t, Zn, NCS, 2Cl	764·2	764·2	
H_2**LV5t** , 2Zn, H	703·2	703·2	703·5
H_3**LV5t** , Zn	639·3	639·3	639·3

In the FAB-ms of **123** ions for fragments of the full ligand incorporating 1 and 2 zincs are seen. The base peak in the mass spectra for both complexes **123** and **124** is for the ligand incorporating only one zinc and only trace amounts of the other peaks are seen. The closest fit to the chemical analysis of **123** is for $[Zn_2(H_4$**LV5t**$)(NCS)_4]\cdot 2CH_3CH_2OH$ and for **124** is $[Zn_2(H_4$**LV5t**$)(NCS)_5]\cdot 3CH_3CH_2OH$ which obviously does not make chemical sense so $[Zn_2(H_4$**LV5t**$)(NCS)_4]\cdot NH_4NCS\cdot 3CH_3CH_2OH$ has been assigned. Neither of these explain the fact that the fragments seen in the FAB-ms of both these complexes appear to contain chloride ions

6 : CONCLUSION

In the absence of any crystal structures of zinc complexes the proposed structures have been assigned based on spectroscopic techniques and chemical analyses. The distinctive binuclear pattern first identified in the infrared spectra of the cobalt complexes has been most helpful in identifying the zinc compounds. For many of the compounds their insolubility in most solvents made it difficult to obtain good mass spectra and this led to experimenting with using the solid samples. This appears to have been very successful and it is unfortunate that time restraints have meant that not all samples have been able to be re-run this way. From the FAB-ms of all the zinc compounds it would appear that many of them are not pure and contain some polymeric compound as well as the structure assigned. This has meant that in some cases although the proposed structure has a reasonable fit to the analysis it may not be as close as is usually deemed to be acceptable. In these

cases the main ions of the mass spectra have been used to justify the assignment.

The perchlorate - **LV5** reactions have yielded a number of binuclear complexes and it is speculated that these are essentially the same in structure as the analogous cobalt structures. In contrast, four tetranuclear complexes have been identified from the **LV5t** reactions.

From the nitrate reactions with either ligand only three complexes have been assigned formulae. All of these are deemed to be tetranuclear. Many more nitrate reactions were tried and the products were mainly insoluble in most solvents. From the mass spectra and the analyses it would appear that most of these are complicated mixtures.

The chloride reactions appear to have yielded (except for complex **117**) only tetranuclear complexes of both **LV5** and **LV5t**.

The only reaction tried with a zinc acetate salt was with **LV5t** and also had thiocyanate added. The two products appear to be binuclear and contain NCS anions.

EXPERIMENTAL - ZINC COMPLEXES

1 : ZINC WITH PERCHLORATE

LV5 Complexes

Complex 102 : $[Zn_2(H_4LV5)Cl_2(OH)(ClO_4)]\cdot CH_3OH$

$Zn(ClO_4)_2\cdot 6H_2O$ (4 mmol, 1·489g) and 2,6-diformyl-4-methylphenol (2 mmol, 0·324g) was dissolved in boiling dry ethanol (50mL). The bright yellow solution was refluxed for 10 min. While continuing to reflux, a solution of 1,5-diamino-3-hydroxypentane made from the dihydrochloride salt (2 mmol, 0·382g) neutralised with KOH (4 mmol, 0·224g) in dry methanol was added dropwise with constant stirring. The bright yellow solution was refluxed for ~ 20 h and left to cool for 48 h. A small amount of deep yellow powder was collected under vacuum, washed with 3 x 5 mL of dry EtOH and dried *in vacuo* overnight.
Yield : 0·157 g, 0·187 mmol, 9·39 %

When this powder was stirred in 50 mL of boiling CH_3CN not all of it dissolved. The mixture was filtered and most of the yellow filtrate set up in ether for recrystallisation. The undissolved residue, a deep yellow cake **102**, was collected from the filter paper.
Yield 0·018 g, 0·022 mmol, 2·2 %.
IR : 3445, 2929, 1661, 1538, 1099, 871, 816, ~770, 623 cm^{-1}.
FAB-ms : 823·1(37), 719·1(83), 619·1(58), 555·2(67), 493·2(100), 473·1(77)
823·0 : H_2**LV5,** 2Zn, ClO_4, OH, H_2O, H
719·1 : H_2**LV5,** 2Zn, ClO_4, 2H

Analysis for : $[Zn_2(H_4$**LV5**$)Cl_2(OH)(ClO_4)]\cdot CH_3OH$

Calculated :	C : 41·43;	H : 4·68;	N : 6·66;
Found :	C : 41·46;	H : 4·42;	N : 6·56;

The remainder of the filtrate of **102** dried to yellow-brown shiny flakes and analysis showed these to be the same product.
Yield : 0·033g, 0·039 mmol, 3·9 %

IR : 3448, 2921, 1653, 1542, 1122, 1087, 863, 813, ~770, 621 cm^{-1}.

FAB-ms : 1290·5(8), 555·2(47), 493·2(100).

Analysis for : $[Zn_2(H_4\mathbf{LV5})Cl_2(OH)(ClO_4)]\cdot CH_3OH$

Calculated :	C : 41·43;	H : 4·68;	N : 6·66 %
Found :	C : 41·41;	H : 4·55;	N : 6·60 %

Complex 103 : $[Zn_2(H_4LV5)(ClO_4)Cl_3]\cdot H_2O$

$Zn(ClO_4)_2\cdot 6H_2O$ (4 mmol, 1·489g) and 2,6-diformyl-4-methylphenol (2 mmol, 0·324g) was dissolved in boiling dry ethanol (50mL). The bright yellow solution was refluxed for 10 min. While continuing to reflux a solution of 1,5-diamino-3-hydroxypentane (2 mmol) , in MeOH : EtOH, was added dropwise with constant stirring. The bright yellow solution was refluxed for ~ 23 h and left to cool overnight. A mid-yellow powder was collected under vacuum, washed with 3 x 5 mL of dry EtOH and dried *in vacuo* overnight. From the FAB-ms and analysis this powder contains a binuclear structure and some other unidentified material.

Yield : 0·122 g, 0·0804 mmol, 8·04 %

IR : 3482, 2925, 1653, 1544, 1088, 940, ~870, 817, ~770, 625 cm^{-1}.

FAB-ms : 719·0 (51), 657(14), 619·1(35), 555·1(68), 493·2(72), 341·2(100).

719·0 : $H_3\mathbf{LV5}$, 2Zn, ClO_4, H^+

619·1 : $H_2\mathbf{LV5}$, 2Zn, H^+

Analysis indicates this product to be a macrocyclic compound with a large amount of various other zinc complexes.

The washings and filtrate of this first product were combined and left to stand. After some time some bright yellow powder **103** coated the walls of the flask and was collected.

Yield : 0·066 g, 0·079 mmol, 7·9 %.

IR : 3440, 2927, 1653, ~1630, 1547, 1108, 872, 817, ~770, 625 cm^{-1}.

FAB-ms : 719·1(70), 619·1(58), 573·1(32), 555·2(100), 493·2(86), 473·1(100)

Analysis for : $[Zn_2(H_4\mathbf{LV5})(ClO_4)Cl_3]\cdot H_2O$

Calculated :	C : 39·79;	H : 4·29;	N : 6·63 %
Found :	C : 39·70;	H : 4·06;	N : 6·47 %

Complex 104 : $[Zn_2(H_4LV5)(OH)(ClO_4)(CH_3OH)_2]\cdot[Zn_2Cl_6]^{2-}\cdot 3H_2O$

$Zn(ClO_4)_2\cdot 6H_2O$ (4 mmol, 1·489g) and 2,6-diformyl-4-methylphenol (2 mmol, 0·324g) was dissolved in boiling dry ethanol (40mL). The bright yellow solution was refluxed for 10 min. While continuing to reflux a solution of 1,5-diamino-3-hydroxypentane (2 mmol), in MeOH : EtOH, was added dropwise with constant stirring. The dark yellow solution was refluxed for ~ 24 h and left to cool overnight. A small amount of a micro-crystalline yellow crust had formed around the solvent line. The mixture was set aside for slow evaporation. After 14 days the product, a brownish-yellow powder **104**, was collected under vacuum, washed with 3 x 5 mL of dry EtOH and dried *in vacuo* overnight.

Yield : 0·300 g, 0·249 mmol, 24·90 %

IR : 3447, 2926, 1626, 1545, 1090, 871, 817, 777, 720, 625 cm^{-1}.

FAB-ms : 788·1(5), 735·0(4), 719·0(52), 619·0(32), 573·1(20), 555·1(48), 493·2(68), 493·2(68), 473·1(100).

788·0 - H_2**LV5**, 2Zn, 2Cl, ClO_4, H^+
735·0 - H_2**LV5,** 2Zn, ClO_4, H_2O
719·1 - H_2**LV5,** 2Zn, ClO_4, 2H
473·1 - H_2**Lo-s**, Zn

Analysis for : $[Zn_2(H_4$**LV5**$)(OH)(ClO_4)(CH_3OH)_2]\cdot[Zn_2Cl_6]^{2-}\cdot 3H_2O$

Calculated :	C : 30·09;	H : 3·96;	N : 4·68 %
Found :	C : 29·94;	H : 3·89;	N : 4·67 %

Complex 105 : $[Zn_2(H_4LV5)(ClO_4)_3Cl]\cdot 4CH_3OH$

The reaction was one in the series using only two metal equivalents. $Zn(ClO_4)_2\cdot 6H_2O$ (2 mmol, 0·746 g) and dfmp (2 mmol, 0·324g) were refluxed in 1 : 1 MeOH : EtOH for 65 mins. While continuing to reflux a solution of dahp (2 mmol), in 10 mL of MeOH : EtOH, was added dropwise with constant stirring. Some solid appeared around the solvent line of the reaction mixture within 2 h of the reaction beginning. The mixture was refluxed for ~ 17 h and left to cool overnight after which a yellow powder, **105**, was collected under vacuum.

Yield : 0·190 g, 0·177 mmol, 17·70 %

IR : 3446, 2926, 1662, 1546, 1088, 870, 817, 773, 718, 625 cm^{-1}.

FAB-ms : 819·0(12), 719·0(100), 655·0(46), 619·0(76), 594(34), 555·1(74), 493·2(100), 473·0(48).

719·0 : H_4**LV5**, 2Zn, ClO_4

Analysis for : $[Zn_2(H_4\mathbf{LV5})(ClO_4)_3Cl]\cdot 4CH_3OH$

Calculated :	C : 35·35;	H : 4·83;	N : 5·19 %
Found :	C : 35·53;	H : 4·39;	N : 4·90 %

Complex 106 : $[Zn_2(H_2\mathbf{Lo\text{-}s})Cl_2(ClO_4)_2]$

The filtrate of **105** was set aside for slow evaporation, dried completely, had dry EtOH added and the undissolved material, a bright yellow powder **106** and some orange crystalline material **107**, were collected and manually separated.

Yield : 0·394 g, 0·490 mmol, 49·00 %.

IR : 3454, 1662, 1643, 1538, 1121(tr), 885, 816, 775, 721, 627 cm^{-1}.

FAB-ms : 636·9(4), 573·0(25), 473·1(100), 444·0(10), 415·0(5), (very clean)

639·9 : H_2**Lo-s**, 2Zn, ClO_4, H^+
573·1 : H_2**Lo-s**, Zn, ClO_4, H^+
473·1 : H_2**Lo-s**, Zn,

Analysis for : $[Zn_2(H_2\mathbf{Lo\text{-}s})Cl_2(ClO_4)_2]$

Calculated :	C : 37·15;	H : 4·07;	N : 3·77 %
Found :	C : 37·16;	H : 4·13;	N : 3·77 %

Complex 107 : $[Zn_2(H_4LV5)(ClO_4)Cl_3]\cdot 2H_2O$

The orange crystalline material separated from the filtrate of **105**.

Yield : 0·060 g, 0·061 mmol, 6·10 %.

IR : 3449, 2926, 1658, 1649, 1537, 1109(tr.), 872, 815, 775, 722, 626 cm^{-1}.

FAB-ms : 757·1(8), 719·1(17), 655·1(18), 619·0(8), 608·9(9), 573·0(39), 554·8(88), 493(43), 473·0(100).

473·0 : H_2**Lo-s**, Zn.
554·2 : H_2**Lo-s**, 2Zn, H_2O, H^+.
573·0 : H_2**Lo-s**, 2Zn, ClO_4, H^+.

Analysis for : $[Zn_2(H_4\mathbf{LV5})(ClO_4)Cl_3]\cdot 2H_2O$

Calculated :	C : 38·87;	H : 4·66;	N : 6·48 %
Found :	C : 39·07;	H : 4·70;	N : 6·77 %

Complex 108 : $[Zn_4LV5(ClO_4)_4]\cdot 4CH_3CH_2OH$

The **106** filtrate dried to a deep yellow cake, dry EtOH was added, and the undissolved yellow fine powder **108** collected.

Yield 0·14 g, 0·105 mmol, 10·5 %.

IR : 3446, 2928, 1662, 1538, 1180, 1145, 1121, 885, 816, 775, 722, 627 cm^{-1}.

FAB-ms : 757(10), 719·0(24), 655·0(33), 619·0(20), 573·0(34), 554·8(89), 490·9(72), 472·4(100).

Analysis for : $[Zn_4\mathbf{LV5}(ClO_4)_4]\cdot 4CH_3CH_2OH$

Calculated :	C : 32·46;	H : 4·21;	N : 4·21 %
Found :	C : 32·95;	H : 4·07;	N : 3·59 %

Complex 109 : $[Zn_4LV5Cl_2(ClO_4)_2]\cdot CH_3CH_2OH\cdot CH_3OH\cdot 5H_2O$

The $Zn(ClO_4)_2$ and dfmp were dissolved in 50 mL of boiling dry ethanol and refluxed for 15 min. The dahp was made in 40 mL of MeOH : EtOH. The yellow solution was refluxed for 24 h and filtered hot to separate a dark yellow powder (**109**).

Yield : 0·800 g, 0·673 mmol, 67·30 %

IR : 3450, 3227, 2926, 1654, sh1637, 1543, 1092, 870, 814, 775, 719, 626.

FAB-ms : 884·9(15), 821·0(50), 782·9(10), 757·0(16), 719·0(100), 657·1(28), 619·0(29), 555·2(70).

All the ions for binuclear complexes

Analysis for : $[Zn_4\mathbf{LV5}Cl_2(ClO_4)_2]\cdot CH_3CH_2OH\cdot CH_3OH\cdot 5H_2O$

Calculated :	C : 28·92;	H : 4·07;	N : 4·35 %
Found :	C : 28·72;	H : 4·26;	N : 4·35 %

LV5t Complexes

Complex 110 : $[Zn_4LV5t(ClO_4)_4]\cdot 8H_2O$

The $Zn(ClO_4)_2$ and dftp were dissolved in 50 mL of boiling dry ethanol and refluxed for 15 min. The dahp was made in 1 :1 MeOH : EtOH. The yellow solution was refluxed for 24 h and filtered hot to separate a little white powder. The yellow solution was kept at room temperature overnight. A tiny amount more of white solid was filtered off, the yellow filtrate concentrated to ~ 5 mL and 100 mL of ether added. A brownish oil separated at the bottom, the mother liquor was decanted off and a further 100 mL of ether added to the oil and the mixture kept at room temperature. The solvent was again filtered off to give a yellowish-brown oil which solidified on drying to give a bright yellow powder (**110**).

Yield : 0·800 g, 0·585 mmol, 58·5 %

IR : 3449, 3217, 2960, 1659, 1541, 1089(tr), 892, 841, 774, 725, 626 cm^{-1}.

FAB-ms : 1048(13), 966·5(47), 945(29), 902·6(66), 866·6(35), 802·7(100), 786·7(19), 740·7(22), 702·8(23), 638·9(25), 602·8(17), 584·7(21), 507·8(32),

492·8(23)

964·0 : **LV5t**, 4Zn, ClO_4, $2H_2O$, H
967·8 : **LV5t**, 3Zn, $2ClO_4$,
945 : **LV5t**, 4Zn, ClO_4, H_2O
864·0 : **LV5t**, 4Zn, $2H_2O$
864·0 : **LV5t**, 3Zn, ClO_4, H

Analysis for : $[Zn_4$**LV5t**$(ClO_4)_4]\cdot 8H_2O$

Calculated :	C : 29·67;	H : 4·39;	N : 4·07 %
Found :	C : 29·58;	H : 4·57;	N : 4·32 %

Complex 111 : $[Zn_4$LV5t$(ClO_4)_4]$

The $Zn(ClO_4)_2$ and dftp were dissolved in 50 mL of boiling dry ethanol and refluxed for 15 min. The dahp was made in 1 :1 MeOH : EtOH. The yellow solution was refluxed for 24 h after which the reaction mixture was taken to dryness under vacuum and CH_3CN added. As all of the product dissolved the stoppered reaction flask was set aside. After considerable time small amount of bright lemon powder **111** was collected in a Hirsch funnel and the bright yellow filtrate set aside for slow evaporation.

Yield : 0·19 g, 0·154 mmol, 15·40 %

IR : 3446, 2925, 1653, 1559, 1096(spl), 899, 875, 816, 770, 625 cm^{-1}.

FAB-ms : 931·7(23), 865·7(100), 800·7(58), 782·7(32), 765(23), 614·8(35),

931·9 : **LV5t**, 4Zn, 2Cl, 2OH
865·7 : **LV5t**, 4Zn, Cl, H
800·1 : **LV5t**, 3Zn, (Cl + H or $2H_2O$) 782·7 : **LV5t**, 3Zn, H_2O

Analysis for : $[Zn_4$**LV5t**$(ClO_4)_4]$

Calculated :	C : 33·15;	H : 3·60;	N : 4·55 %
Found :	C : 32·91;	H : 3·72;	N : 4·88 %

Complex 112 : $[Zn_4$LV5t$(ClO_4)_4]\cdot CH_3CH_2OH$

The dried filtrate of **111** had water added and a bright yellow solid (**112**) appeared. This was collected under vacuum and washed with H_2O.

Yield 0·60 g, 0·473 mmol, 47·3 %

IR : 3441, 2918, 2858, 1651, 1543, 1109, 1088, 984, 874, 810, 772, 621 cm^{-1}.

FAB-ms : 864·6(100), 845(31), 801(51), 783(60), 765(38), 719(50), 615(62), 450·8(84), 423·8(96)

Analysis for : $[Zn_4$**LV5t**$(ClO_4)_4]\cdot CH_3CH_2OH$

Calculated :	C : 33·83;	H : 3·94;	N : 4·38 %
Found :	C : 33·84;	H : 3·68;	N : 4·21 %

Complex 113 : $[Zn_4LV5t(OH)(ClO_4)_3]\cdot TEA\cdot CH_3CH_2OH$

$Zn(ClO_4)_2$and dftp was dissolved in boiling dry ethanol and the pale yellow solution refluxed for 30 min. When the dahp solution was added the solution became a deep gold. The solution was refluxed for ~ 24 h and left to cool overnight. Solid now encrusted the walls of the flask. This bright lemon yellow micro-crystalline material **113** was collected by vacuum filtration.

Yield 0·51 g, 0·464 mmol, 46·4 %.

IR : 3439, 2960, 2863, 1652, 1549, 1093(mult), 977, 899, 832, 774, 622 cm^{-1}.

FAB-ms :1174·6(7), 946·6(35), 882·6(100), 866(42), 850·6(22), 802·7(65), 791 (17), 700·8(32).

946·6 : H_2**LV5t** , 4Zn, TEA, OH
882·0 : H_2**LV5t** , 3Zn, TEA, OH
866·2 : H_2**LV5t** , 3Zn, TEA

Analysis for : $[Zn_4$**LV5t**$(OH)(ClO_4)_3]\cdot TEA\cdot CH_3CH_2OH$

Calculated :	C : 39·38;	H : 5·19;	N : 5·47 %
Found :	C : 39·20;	H : 4·98;	N : 5·30 %;

2 : ZINC WITH NITRATE

LV5 Complexes

Complex 114 : $[Zn_4LV5(NO_3)_2Cl_2]\cdot 4H_2O$

The $Zn(NO_3)_2$ and dfmp were dissolved in 50 mL of MeOH and refluxed for 10 min. Dahp, in 25 mL of 1 : 1 MeOH : EtOH was added, followed by 1 mL of TEA (a little over 6 mmol). A turbidity formed immediately. The mixture was refluxed for 24 h and a pale yellow powder **114** separated. This was collected by vacuum filtration, washed with 3 x 5 mL of MeOH and dried *in vacuo.*

Yield : 0·180 g, 0·178 mmol, 17·80 %

IR : 3429, 2916, 2856, 2426, 1647, 1556, 1451, 1384, 1322, 1304, 969, 928, 890, 813, 772, 613 cm^{-1}.

FAB-ms : 1116·0(11), 1089·0(9), 1024(11), 999·0(17), 917·0(10), 888·9(12), 863·9(18), 825·9(100), 798·9(93), 764·9(22), 701·0(14).

1115·8 : **LV5**, 4Zn, $6NO_3$
1088·9 : **LV5**, 4Zn, $5NO_3$, Cl
1026·9 : **LV5**, 4Zn, $4NO_3$, Cl
999·9 : **LV5**, 4Zn, $3NO_3$, Cl

Analysis for : $[Zn_4\mathbf{LV5}(NO_3)_2Cl_2]\cdot 4H_2O$

Calculated :	C : 33·07;	H : 3·96;	N : 8·26 %
Found :	C : 32·86;	H : 3·62;	N : 8·02 %

Complex 115 : $[Zn_4LV5(NO_3)_2Cl_2]\cdot 2CH_3OH\cdot 2H_2O$

The filtrate of complex **114** was set aside for slow evaporation. A pale yellow powder (complex **115**) was collected from this.

Yield : 0·13 g, 0·124 mmol, 12·4 %

IR : 3421, 2918, 2855, 1767 (tiny), 1652, 1557, 1384, 1327, 967, 893, 813, 770 cm^{-1}.

FAB-ms : 920·9(25), 825·9(72), 798·9(54), 780·9(64), 763(45), 615(92), 503·9(58), 450·9(93), 421·9(100)

920·9 : **LV5**, 4Zn, $2NO_3$, Cl, H_2O
823·9 : **LV5**, 4Zn, NO_3, H_2O
796·9 : **LV5**, 4Zn, Cl, H_2O
778·9 : **LV5**, 4Zn, Cl

Analysis for : $[Zn_4\mathbf{LV5}(NO_3)_2Cl_2]\cdot 2CH_3OH\cdot 2H_2O$

Calculated :	C : 34·48;	H : 4·24;	N : 8·04 %
Found :	C : 34·55;	H : 4·38;	N : 7·76 %

LV5t Complexes

Complex 116 : $[Zn_4LV5t(NO_3)Cl_3]\cdot HTEA^+Cl^-$

The $Zn(NO_3)_2$ and dftp were dissolved in 100 mL of MeOH and refluxed for 15 - 20 min. Dahp, in 20 mL of 2 : 1 MeOH : EtOH was added in two aliquots. TEA (4 mmol) was also added. The mixture was refluxed for 24 h and a very pale yellow powder **116** separated. This was collected by vacuum filtration, washed with 3 x 10 mL of EtOH and dried *in vacuo.*

Yield : 0·70 g, 0·613 mmol, 61·30 %

IR : 3447, 2953(2), 2864, 2808, 1645, 1553, 1384(v wk), 883, 859, 835, 816, 774 cm^{-1}.

FAB-ms : 1197·9(21), 999·9(5), 911·9(100), 848·9(56), 832·9(20), 698·9(49), 683(44).

1197·1 : **LV5t**, 4Zn, $4NO_3$, TEA, H_2O, H^+
698·2 : **LV5t**, Zn, NO_3.
698·1 : **Lo-st**, 2Zn, NO_3, OH
683·1 : **Lo-st**, Zn, NO_3.

Analysis for : $[Zn_4\mathbf{LV5t}(NO_3)Cl_3]\cdot HTEA^+Cl^-$

Calculated :	C : 42·10;	H : 5·39;	N : 7·36 %
Found :	C : 41·03;	H : 4·84;	N : 7·40 %

3 : ZINC WITH CHLORIDE

LV5 Complexes

Complex 117 : $[Zn_3(HLV5)Cl_3]\cdot H_2O\cdot 2CH_3OH$

The $ZnCl_2$ and dfmp were dissolved separately in 20 mL of dry EtOH each, combined and refluxed for 10 min. $DahpCl_2$ was dissolved in 20 mL of dry MeOH, 45 mL of previously prepared KOH solution (in MeOH) was added to this and the mixture sat in ice for 2 h to precipitate the KCl. The first part of the dahp solution was added through a filter and over an hour later (after a super long seminar) the rest was added by which time a significant amount of bright

yellow powder had already formed in the reaction mixture. After refluxing a further 20 h the bright yellow powder **117** was collected by vacuum filtration from the hot mixture, dried *in vacuo* for 2 h, and left to air dry for 2 days.

Yield : 0·65 g, 0·750 mmol, 75·00 %

IR : 3447, 2924, 1653, 1635, 1545 870, 817, 776 cm^{-1}.

FAB-ms : 683(31), 655·0(67), 629(54), 555·1(94), 507(40), 468·0(100).

68 : H**LV5**, 3Zn, H
655·0 : H_2**LV5**, 2Zn, Cl, H
555·1 : H_3**LV5**, Zn.

Analysis for : $[Zn_3(H_2\mathbf{LV5})Cl_3]\cdot H_2O\cdot 2CH_3OH$

Calculated :	C : 41·27;	H : 4·85;	N : 6·42 %
Found :	C : 41·25;	H : 4·79;	N : 6·61 %

Complex 118 : $[Zn_4\mathbf{LV5}(OH)_2Cl_2]\cdot H_2O$

The $ZnCl_2$ and dfmp were dissolved in 100 mL of dry EtOH and refluxed for 15 - 20 min. Dahp, in 20 mL of 2 : 1 MeOH : EtOH, was added in 2 aliquots. TEA (4 mmol) was also added. A turbidity formed immediately. A pale yellow powder **118** separated. This was collected by vacuum filtration, washed with 3 x 10 mL of EtOH and dried *in vacuo.*

Yield : 0·60 g, 0·687 mmol, 68·70 %

IR : 3493, 2915, 1651, 1555, 887, 813, 771 cm^{-1}.

FAB-ms :1089·0(38), 971·9(64), 800·8(100), 718·9(37), 615(30), 566·9(69), 530·9(39), 423·9(32).

1089·7 : **LV5**, 4Zn, O, 2Cl, 2OH + (2Zn, 2Cl, OH)
971·9 : **LV5**, 4Zn, O, 2Cl, 2OH + Zn, Cl
801·7 : **LV5**, 4Zn, O, Cl

Analysis for : $[Zn_4\mathbf{LV5}(OH)_2Cl_2]\cdot H_2O$

Calculated :	C : 38·52;	H : 4·16;	N : 6·42 %
Found :	C : 38·71;	H : 4·24;	N : 6·43 %

LV5t Complexes

Complex 119 : $[Zn_4LV5tCl_4]\cdot 4CH_3CH_2OH$

The $ZnCl_2$ and dftp were dissolved in 50 mL of boiling dry ethanol and refluxed for 15 min. The dahp was made in 1 :1 MeOH : EtOH. A reddish oily material was formed on the walls and some yellow solid on the bottom of the flask. The yellow mother liquor was decanted off and left for slow evaporation. The bright yellow solid **119** which was left was washed with EtOH.

Yield : 0·308 g, 0·266 mmol, 26·6 %

IR : 3439, 2956, 1657, 1635, 1542, 1232, 958, 885, 840, 776 cm^{-1}.

FAB-ms : 883·0(23), 839·0(50), 801·0(33), 775·1(78), 739·2(100), 703(47), 639·2(71), 620·2(48), 576·2(90),

881·0 : **LV5t**, 4Zn, Cl, H_2O
837·0 : **LV5t**, 3Zn, 2Cl, H

Analysis for : $[Zn_4\mathbf{LV5t}Cl_4]\cdot 4CH_3CH_2OH$

Calculated :	C : 43·47;	H : 5·91;	N : 4·83 %
Found :	C : 43·76;	H : 5·53;	N : 4·85 %

Complex 120 : $[Zn_4LV5t(dftp)_2(NCS)_2Cl_2]\cdot NH_4^+NCS^-\cdot NH_4^+Cl^-$

The filtrate of **119** was set aside for slow evaporation and after 2 weeks yielded a yellow powder (**120**).

Yield : 0·519 g, 0·333mmol, 33·30 %

IR:3433, 2961, 2910, 2866, 2077, 1655, 1582, 1556, 980, 891, 831, 775 cm^{-1}.

FAB-ms : 1198·1(20), 1103·0(43), 1096·0(19), 1070·0(15), 969·0(16), 908·0(100), 890·0(31), 867·0(25), 849·0(38), 826·0(19), 701·0(26).

Analysis : $[Zn_4\mathbf{LV5t}(dftp)_2(NCS)_2Cl_2]\cdot NH_4^+NCS^-\cdot NH_4^+Cl^-$

Calculated :	C : 46·92;	H : 5·04;	N : 8·07 %
Found :	C : 46·92;	H : 5·05;	N : 8·35 %

Complex 121 : $[Zn_4LV5tCl_4]\cdot 2CH_3CH_2OH$

The $ZnCl_2$ and dftp were dissolved in 50 mL of dry EtOH and the pale yellow solution refluxed for 30 min. Dahp was added and a yellow solid appeared. The mixture was refluxed a further 30 mins then TEA (4 mmol) was also added. The reaction mixture was refluxed 24 h. A yellow powder (**121**) was collected by vacuum filtration, and dried *in vacuo.*

Yield : 0·59 g, 0·552 mmol, 55·20 %

IR : 3441, 2956, 2865, 1649, 1551, 973, 895, 832, 775 cm^{-1}.

FAB-ms : 1281·1(6), 1173·1(19), 1056·0(40), 941·0(13), 921·0(20), 885·0(100), 803·1(50), 657·1(35), 508·1(43).

Analysis for : $[Zn_4$**LV5t**$Cl_4]\cdot 2CH_3CH_2OH$

Calculated :	C : 42·73;	H : 5·28;	N : 5·24 %
Found :	C : 42·61;	H : 5·02;	N : 5·01 %

Complex 122 : $[Zn_4$ LV5t$Cl_4(dftp)_2]\cdot 4H_2O$

The dried filtrate of **121** had EtOH added and the undissolved yellow powder **122** collected.

Yield : 0·12 g, 0·080 mmol, 8·0 %.

IR : 3439, 2960, 1646, 1548.

FAB-ms : 1284·2(8), 1177·4(5), 1044·2(6), 975·0(11), 929·1(13), 883·0(18), 805·1(15), 759·0(26), 741·1(18), 657·0(100), 557·1(91), 510·0(97).

Analysis for : $[Zn_4$ **LV5t**$Cl_4(dftp)_2]\cdot 4H_2O$

Calculated :	C : 47·76;	H : 5·39;	N : 3·84 %
Found :	C : 47·69;	H : 5·20;	N : 3·58 %

4 : ZINC WITH ACETATE

LV5t Complexes

Complex 123 : $[Zn_2(H_4$LV5t$)(NCS)_4]\cdot 2CH_3CH_2OH$

The $Zn(OAc)_2$ and dftp were dissolved in 50 mL of boiling dry ethanol and refluxed for 15 min. The dahp was made in 1 :1 MeOH : EtOH. After adding NH_4NCS to the yellow solution a turbidity appeared and after some time a fluffy precipitate. The reaction mixture was refluxed for 24 h and some orange solid **123** was filtered from the hot solution.

Yield: 0·15 g, 0·145 mmol, 14·5 %.

IR:3433, 2952, 2865, 2085, 1663, 1637, 1526, 1229, 976, 955, 887, 681 cm^{-1}.

FAB-ms : 930·4(3), 828·3(6), 764·2(6), 703·2(8), 655·3(7), 639·3(100), 577·3(31), 478·2(16).

Analysis : $[Zn_2(H_4\mathbf{LV5t}(NCS)_4]\cdot 2CH_3CH_2OH$

Calculated :	C : 48·98;	H : 5·68;	N : 10·98 %
Found :	C : 50·56;	H : 5·43;	N : 11·18 %

Complex 124 : $[Zn_2(H_4LV5t)(NCS)_5]\cdot 3CH_3CH_2OH$.

The yellow filtrate of **123** was kept at room temperature for slow evaporation and gave a bright yellow powder **124** which was washed with 3 x 3 mL of dry EtOH and dried *in vacuo*.

Yield : 0·439 g, 0·387 mmol, 38·7 %

IR : 3433, 2953, 2866, 2077, 1663, 1637, 1527, 976, 955, 887, 681 cm^{-1}.

FAB-ms : 703·5(20), 639·4(100), 441·2(43), 423·2(83), 402·1(85)

The closest analysis is for $[Zn_2(H_4\mathbf{LV5t})(NCS)_5]\cdot 3CH_3CH_2OH$

Calculated :	C : 47·66;	H : 5·69;	N : 11·11;	S : 14·14 %
Found :	C : 51·81;	H : 5·45;	N : 11·02;	S : 13·83 %

but this obviously does not make chemical sense.

Analysis : $[Zn_2(H_4\mathbf{LV5t})(NCS)_4]\cdot NH_4NCS\cdot 3CH_3CH_2OH$.

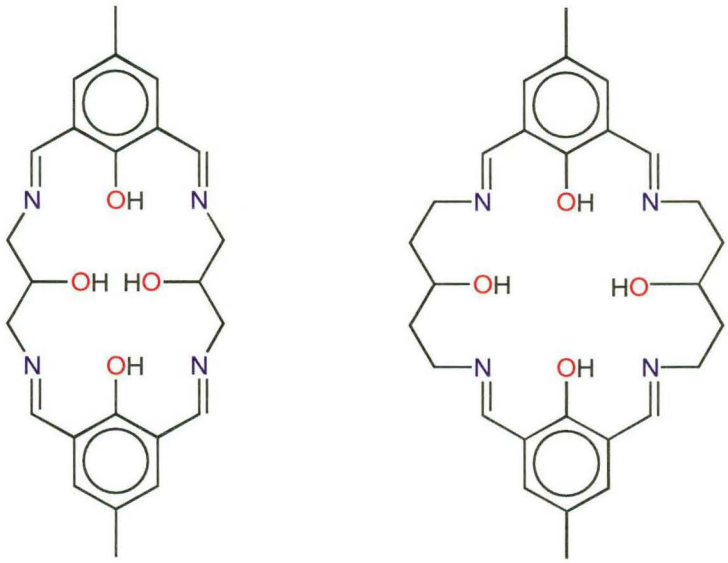
Calculated :	C : 46·83;	H : 6·11;	N : 12·14;	S : 13·89 %
Found :	C : 51·81;	H : 5·45;	N : 11·02;	S : 13·83 %

CHAPTER 9

THE LEAD, BARIUM and IRON COMPLEXES

1 : INTRODUCTION

In this chapter the lead, barium and iron syntheses are discussed. The perchlorate salts of these three metals were used in syntheses that were part of a "Binuclear Series" in which only two equivalents of the metal were used. In addition to these, a number of other syntheses, using iron were undertaken.



LV3 **LV5**

Figure 9·1 : The LV3 and LV5 ligands

A series of **LV5** (Fig 9·1) syntheses (the so-called "Binuclear Series"), in which only two equivalents of the metal salt were used, was carried out. In these syntheses Cu(II), Co(II), Mn(II), Ni(II), Zn(II), Pb(II), Ba(II), and Fe(II), were the templating metals and with the exception of cobalt, only the perchlorate salt of these metals was used. For cobalt, thiocyanate, acetate, and nitrate salts were used in addition to the perchlorate. It was hoped that binuclear complexes of **LV5** would be formed and the characteristics of these could be compared and

contrasted with those made with the **LV3** (Fig 9·1) ligand. Of particular interest was the disposition of the metals within the macrocycle and whether the alcohol groups would be deprotonated or not. The products of the copper, cobalt, manganese, nickel and zinc syntheses have been discussed in the preceding chapters.

Complexes of the **LV3** ligand, formed from the [2 +2] template condensation of 2,6-diformyl-4-methylphenol and 1,3-diamino-propan-2-ol with salts of lead[42], barium[42], copper[46], manganese[48] and nickel[48], have been discussed in Chapter One (pp. 46 - 52). Structurally, the Ni(II), Mn(II), and Cu(II) were similar to the **L3-3** complexes with two metal ions bridged by the deprotonated phenolate donors of the macrocycle and the alcohol groups retaining their protons and not coordinated to the metal ions. In the $[Pb_2(H_2\mathbf{LV3})]\cdot(ClO_4)_2$ complex (Fig 9·2) the alcohol groups are protonated and coordinated to the lead ions but the length of this bond indicates that this is a weak interaction. A mononuclear lead complex was also characterised. Only mononuclear barium complexes were isolated.

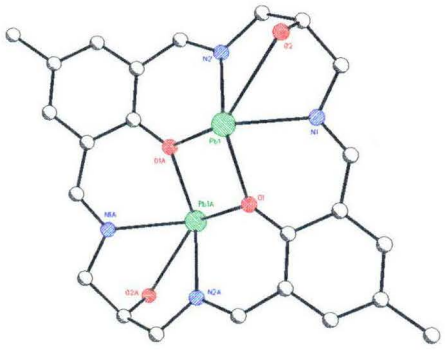


Figure 9·2 : The $[Pb_2(H_2LV3)]^{2+}$ cation

2 : LEAD

Solid product started appearing within 10 minutes of the start of refluxing in lead synthesis carried out in this series. The mixture was refluxed for a further 60 minutes and left to cool overnight and the product collected as a fine bright yellow powder. A comparison with the peak pattern established for the cobalt complexes showed that features in IR of this powder were indicative of a tetranuclear complex (complex **125**) having been formed. The assignment of

The filtrate of complex **125** dried, had EtOH added and the undissolved fine bright yellow powder (complex **126**) collected. In the IR of this product a peak pattern similar to that seen for previously identified binuclear complexes was seen but the FAB-ms results (Table 9·1) indicate that a very small amount of a tetranuclear is also present. The bulk of the sample is a binuclear product and the closest formulation to the microanalysis results is $[Pb_2(H_4\mathbf{LV5}(ClO_4)Cl_3]$.

Table 9·1 :
Selected ions (FAB-ms) for the Lead complexes

		125	**126**
LV5, 4Pb, 2Cl, $2ClO_4$	1587·98	1584·1	
LV5, 4Pb, O, $2ClO_4$	1534·04	1532·0	
LV5, 4Pb, $2ClO_4$	1518·04		1521·3
LV5, 4Pb, 2Cl, ClO_4	1489·04	1488	
LV5, 4Pb, O, ClO_4	1435·09	1433·0	
LV5, 4Pb, ClO_4	1419·10		1420·2
LV5, 4Pb, O,	1336·14	1334·1	
LV5, 3Pb, O, Cl	1163·14		1164
LV5, 3Pb, Cl	1147·14	1143	
LV5, 3Pb, O	1128·17	1125·1	
LV5, 2Pb, ClO_4	1102·09		1101
LV5, 2Pb, 2Cl, ClO_4	1073·08	1069·1	
LV5, 2Pb, Cl, ClO_4	1038·11	1039	
LV5, 2Pb, ClO_4	1003·14	1005	1003
LV5, Pb, 2Cl, $2ClO_4$	964·05	966	
LV5, 2Pb, O	920·19		917·1
LV5, Pb, $2ClO_4$	894·11	896	
LV5, Pb, 2Cl, ClO_4	865·1	866	864·2
H_3**LV5**, Pb, ClO_4	798·19	798	
LV5, Pb, 2Cl	766·14		764
H_3**LV5**, Pb, O	712·21		711·1
H_3**LV5**, Pb	699·24	699·2	
H_4**LV5**, ClO_4	591·22	591	
H_4**LV5**, Cl	527·24	527	
H_4**LV5**	492·27	493	494

3 : BARIUM

The barium reaction mixture was refluxed for 21 h and a mixture of an orange-yellow powder and a darker crystalline material (**127**) filtered from the cooled reaction mixture. The filtrate evaporated, EtOH was added and the undissolved orange solid (**128**) filtered off. It was expected that, because of the size of the barium ion, binuclear complexes would be the most likely products of this synthesis. Mass spectral evidence (Table 9·2) indicates that this is the case. However, **128** also has fragments indicative of trace amounts (1 - 2 %) of a tetranuclear complex being present.

Table 9·2 :
Selected ions (FAB-ms) for the Barium complexes

		127	128
LV5, 4Ba, 2Cl, ClO_4, H_2O	1226·76		1228·9
LV5, 4Ba, ClO_4	1138·81		1139·2
LV5, 3Ba, O, ClO_4	1016·90		1016·1
LV5, 2Ba, Cl, $2ClO_4$	996·91		993·1
H_2**LV5**, 2Ba, H_2O, $2ClO_4$	981·97		982·9
LV5, Ba, 2Cl, $2ClO_4$	893·98	893·1	893·1
H_2**LV5**, 2Ba, OH, ClO_4	882·01		882·8
LV5, Ba, 2Cl, ClO_4	795·03	793·2	
H_2**LV5**, 2Ba, OH	783·07		782·9
H_2**LV5**, 2Ba	766·07	766·2	
H_3**Lo-s**, Ba, $2ClO_4$	745·98		747·1
H_4**LV5**, Ba, OH, ClO_4	746·13		
H_2**Lo-s**, Ba, OH	701·98	703	702·0
H_2**Lo-s**, Ba, ClO_4	646·03	646	647·0
H_4**LV5**, Ba, OH	647·18		
H_2**LV5**, 3Cl	595·16	595·2	
H_2**Lo-s**, Ba	547·08	547·1	547·0
LV5	492·27	493·2	

No specific formula has been assigned to **127** as although the consistency of the microanalysis results indicate that the product is homogenous, it appears that some moiety other than the macrocyclic complex is present. Microanalysis results for complex **128** agree with the formulation of $[Ba_2(H_4$**Lo-s**$)(ClO_4)_4]$ $\cdot 3H_2O \cdot CH_3OH$. This is supported by the base peak in the FAB-ms ($^m/_e$) being for an open-sided complex.

4 : IRON

A number of iron syntheses was tried. The first of these was one of the "binuclear series" but for all the others four metal equivalents of the metal salt were used with both Fe(II) and Fe(III) starting materials. Only the perchlorate salts were used. Some of the reaction mixtures were exposed to the air during the reflux period and others were done under nitrogen. Most of the products are mixtures and many appear to contain non-macrocyclic iron complexes of some kind. FAB-ms of these products indicate that macrocyclic complexes are also present. Three complexes have been assigned formulae. Crystals were isolated from one synthesis involving Fe(III). As the crystals were a golden brown colour it was thought that a macrocyclic complex may have been achieved and an X-ray structure analysis was carried out. The structure revealed that the diformyl phenol starting material had been oxidised by the Fe(III) to the dicarboxylic phenol. The crystal structure is discussed in Chpt. 11.

Table 9·3 : The Iron Complexes

129	$[Fe_4\mathbf{LV5}(NCS)_4]\cdot 4H_2O + Fe(NCS)_2$
130	$[Fe(II)_2(H_2\mathbf{Los})(ClO_4)_2Cl(OH)]\cdot H_2O$
131	$[Fe(II)_4\mathbf{LV5}(ClO_4)_4]\cdot 7H_2O\cdot CH_3OH$

Complex **129** was isolated from a reaction mixture in which only two equivalents of iron(II) perchlorate was used. Initially the deep maroon mixture yielded a buff coloured powder which IR showed to be inorganic. NaSCN dissolved in MeOH was added to the filtrate which was then set aside for slow evaporation. A rust coloured powder was isolated from this. There is no indication, in the IR, as to the nuclearity of this product but microanalytical data and FAB-ms (Table 9·4) indicates that this product is a homogenous mixture of a tetranuclear complex, $[Fe_4\mathbf{LV5}(NCS)_4]\cdot 4H_2O$, and $Fe(NCS)_2$. Certainly the product is not binuclear.

Complex **130** was isolated from a reaction mixture in which four equivalents of $Fe(II)(ClO_4)_2$ was the starting material and the synthesis was carried out under a nitrogen atmosphere. The deep red-brown microcrystalline product was pipetted from the reduced reaction mixture. The microanalysis of this product most closely fits the formulation of an open-sided complex, and fragments supporting this are seen in the FAB-ms. The peak at 1669 cm^{-1} (indicative of

carbonyl) seen in the IR of this complex also support this. The formula $[Fe(II)_2(H_2\mathbf{Los})(ClO_4)_2Cl(OH)]\cdot H_2O$ has been assigned to complex **130**. However, the FAB-ms also indicates that a very small amount of a tetranuclear complex has formed.

Table 9·4 : Selected ions (FAB-ms) for the Iron complexes

		129	**130**	**131**
LV5, 4Fe, $3ClO_4$, OH	1027·33		1029·1	
LV5, 4Fe, ClO_4, 4Cl	953·24			956
LV5, 3Fe, $3ClO_4$	954·48			
LV5, 4Fe, Cl, $2ClO_4$	944·84		945·1	
H_2**LV5**, 2Fe, $2ClO_4$, 4Cl	943·01			
LV5, 4Fe, $2ClO_4$, OH	927·88	927·9	929·1	
LV5, 3Fe, $2ClO_4$, Cl	890·48			889
LV5, 4Fe, 5Cl	889·24			
LV5, 2Fe, $2ClO_4$, 2Cl, OH	887·10			
LV5, 4Fe, 2NCS, O	843·93	843		
LV5, 3Fe, ClO_4, 2Cl	826·48			824·0
LV5, 3Fe, ClO_4, Cl	791·03			789
LV5, 4Fe, 2Cl	781·91	779·0		
LV5, 3Fe, 3Cl, OH	779·49			
H_4**LV5**, 2Fe, ClO_4, 2Cl	774·67			773
H_4**LV5**, 2Fe, ClO_4, Cl, OH	756·22	757		753·0
H_4**LV5**, 2Fe, H_2O, ClO_4	721·10	723		
LV5, 3Fe, Cl, OH	708·02			708·0
LV5, 2Fe, 3Cl	706·64			
LV5, 2Fe, 2Cl, OH	687·05		678·0	
LV5, Fe, 2NCS	660·12	658		
H_4**LV5**, 2Fe, Cl, OH	656·77			
H_2**Lo-s**, 2Fe, ClO_4, Cl	656·06			
H_4**LV5**, 2Fe, Cl	639·11	640·0		636·0
H_4**LV5**, 2Fe, H_2O	622·15	623·0		
H_2**Lo-s**, 2Fe, ClO_4	619·99		619	
H_4**LV5**, Fe, 2Cl	618·15			
H_2**Lo-s**, Fe, OH, Cl, ClO_4	617·22			
LV5, 2Fe, OH	617·11			
LV5, 2Fe	600·11	600·0		600·0
H_2**Lo-s**, Fe, O, 3Cl	588·68		586	
H_4**LV5**, Fe, $2H_2O$	584·23			
H_4**LV5**, Fe, OH	565·2	569	565	565·0
H_2**Lo-s**, Fe, ClO_4	564·76			
H_4**LV5**, Fe	548·2			
H_2**Lo-s**, Fe, O, Cl	516·01	515·1		516·0
H_2**Lo-s**, Fe, O	481·11		481·0	
H_2**Lo-s**, Fe	465·11		465·0	465·0

The synthesis using $Fe(II)(ClO_4)_2$ in a nitrogen atmosphere was repeated but on the second occasion the reaction mixture was more dilute. The mixture was refluxed, cooled and allowed to sit for 2 days after which time a fine brown powder was collected. FAB-ms of this product shows that it contains some of an open-sided complex and a smaller amount of a tetranuclear one. The IR is dominated by perchlorate peaks and the microanalysis shows that this is an homogenous mixture with a lot of metal salt being present. The filtrate was set aside and allowed to reduce and then EtOH added. A black crusty solid (complex **131**) was collected from this. This product has been assigned the formula $[Fe_4\mathbf{LV5}(ClO_4)_4]\cdot 7H_2O\cdot CH_3OH$ based on microanalysis and fragments seen in the FAB-ms.

EXPERIMENTAL

1 : LEAD

Complex 125 : $[Pb_4LV5(ClO_4)_2Cl_2]$

The reaction was done with two metal equivalents as part of a series of reactions trying to make binuclear complexes of **LV5**. The 2 mmol dahp solution was made by dissolving dahp·Cl_2 and KOH separately in 10 mL dry MeOH : EtOH and added to a solution of $Pb(ClO_4)_2$ (2 mmol, 0·92 g) and dfmp (2 mmol, 0·324 g) which had been refluxing in dry EtOH (40 mL) 10 mins. A yellow solid formed in the solution within 10 mins of the dahp being added. The mixture was refluxed for a further 60 mins and allowed to cool to overnight. A lot of fine bright yellow powder (Complex **125**) was collected by vacuum filtration and allowed to air dry overnight.

Yield : 0·98 g, 0·617 mmol, 62 %

IR : 3441, 2920, 1637, 1530, 1109, 1090, 625.

FAB-ms ($^m/_e$) : 1488(8), 1432(25), 1332(8), 1039(8), 1005(15), 966(11), 905(13), 866(9), 799(52), 699(100), 666(31), 527(21), 493(97). Belfast

FAB-ms ($^m/_e$) : 1584·1 (3), 1532·0(1), 1486·1(10), 1433·0(100), 1334·1(18), 1143(2), 1125·1(15), 1069·1(9), 1043·1(15), 896(4), 798(4), 699·2(7), 667(14), 591(16), 493(15).

U.V. : 363 (sh) (0·3731), 391 (5098)

Analysis for $[Pb_4\mathbf{LV5}(ClO_4)_2Cl_2]$

Calculated:	C : 21·19;	H : 2·03;	N : 3·53 %
Found:	C : 21·18;	H : 2·07;	N : 3·27 %

Complex 126 : $[Pb_2(H_4LV5(ClO_4)Cl_3]$

The dried filtrate of **125** had EtOH added and the undissolved fine bright yellow powder (complex **126**) collected.

Yield : 0·24 g, 0·198 mmol, 20 %

IR : 3440, 1647, 1539, 1122, 1109, 626.

FAB-ms ($^m/_e$) : 1292(1), 1164(1), 1101(1), 1003(2), 915(2), 863(2), 797(2), 764(2), 711(30), 647(7), 549(3), 494(13), 449(13), 611(100). Belfast

FAB-ms ($^{m}/_{e}$) : 1521·3(1), 1420·2(1), 917·1(1), 864·2(), 711·1(22), 611·2(100), 582·1(5), 493(8) Canterbury

U. V. : 406(1·05)

Analysis for : $[Pb_2(H_4\mathbf{LV5}(ClO_4)Cl_3]$

Calculated:	C : 30·22;	H : 3·26;	N : 5·03 %
Found:	C : 28·70;	H : 3·14;	N : 5·23 %

2 : BARIUM

Complex 127

The reaction was done with two metal equivalents as part of a series of reactions trying to make binuclear complexes of **LV5**. The 2 mmol dahp solution was made by dissolving dahp·Cl_2 and KOH separately in 10 mL dry 1 :1 MeOH : EtOH and added to a solution of $Ba(ClO_4)_2$ (2 mmol, 0·89 g) and dfmp (2 mmol, 0·324 g) which had been refluxing in 40 mL 1 :1 dry MeOH : EtOH 60 mins. Problems with the refluxing meant that after ~ 45 mins ~ 20 mL of the solvent had been lost and a deep orange crust had appeared around the solvent line. A further 20 mL of MeOH was added and the mixture refluxed. After 20 h a solid had formed in the orange solution. The mixture was refluxed for a further 60 mins and allowed to cool to overnight. This product, an orange-yellow powder mixed with some darker crystalline material (complex **127**) was collected by vacuum filtration from the hot solution.

Yield : 0·29 g, 0·28 mmol, 28 %

IR : 3422, 1647, 1529, 1143, 1109, 1089, 636, 626.

Weak macrocyclic backbone.

FAB-ms ($^{m}/_{e}$) : 893·1(3), 839·3(2), 793·2(89), 766·2(4), 739(8), 705?(4), 641(11), 613·2(22), 595·2(17), 547·1(38),493·2(100)

U.V. : 350 (0·81), 450 (0·84)

Analysis for :

Calculated:	C :;	H :;	N : %
Found:	C : 17·49;	H : 1·80;	N : 2·20 %

Complex 128 : $[Ba_2(H_4Lo\text{-}s)(ClO_4)_4]\cdot 3H_2O\cdot CH_3OH$

The filtrate of **127** dried to a bright orange crust, dry EtOH was added and the undissolved orange solid (complex **128**) collected.

Yield : 0·86 g, 0·833 mmol, 83 %

IR : 3445, 1652, 1645, 1634, 1532, 1088, 625

FAB-ms ($^m/_e$) : 1228·9(3), 1139·2(2), 1016·1(2), 993·1(8), 982·9(3), 893·1(15), 882·8(), 782·9(13), 747·1(13), 702·0(13), 647·0(100), 547·0(34),

U. V. : 341(0·3377)

Analysis for : $[Ba_2(H_4$**Lo-s**$)(ClO_4)_4]\cdot 3H_2O\cdot CH_3OH$

Calculated:	C : 28·48;	H : 3·58;	N : 2·77 %
Found:	C : 28·44;	H : 3·73;	N : 2·83 %

3 : IRON

Complex 129 : $[Fe_4LV5(NCS)_4]\cdot 4H_2O + Fe(NCS)_2$

The reaction was done with two metal equivalents as part of a series of reactions trying to make binuclear complexes of **LV5**. The 2 mmol dahp solution was made by dissolving dahp·Cl_2 and KOH separately in 10 mL dry 1 :1 MeOH : EtOH and added to a solution of $Fe(ClO_4)_2$ (2 mmol, 0·73 g) and dfmp (2 mmol, 0·324 g) which had been refluxing in 40 mL 1 :1 dry MeOH : EtOH 20 mins. The mixture, which was a very dark red-brown colour, was refluxed for 24 h and allowed to cool to overnight. As very fine microcrystalline particles were forming on the walls of the flask it was left to sit for a further 5 days. Vacuum filtration of this deep maroon mixture yielded a buff coloured powder (0·08 g) which was shown, by IR, to be inorganic.

The filtrate had NaSCN dissolved in dry MeOH added and was set aside for slow evaporation. After some time the solution had reduced to a deep red sludge from which a rust coloured powder (complex **129**) was collected.

Yield 0·86·g, 0·724 mmol, 72 %

IR : 3441, 2052, 1655, 1627, 1549, 1122. (weak backbone)

FAB-ms ($^m/_e$) : (dominated by NOBA peaks) 843(2), 757(2), 735(3), 657(3), 600(4), 566(3), 547(2), 515(3), 413(100) Belfast

FAB-ms ($^m/_e$) : 779·0(20), 723(18), 632(33), 658(24), 640·0(24), 623·0(52), 600·0(71), 569(31), 515·1(100).

U. V. : 334 (1·05), 396 (1·327), 465 (1·350)

Analysis for : $[Fe_4$**LV5**$(NCS)_4]\cdot 4H_2O + Fe(NCS)_2$

Calculated:	C : 34·36;	H : 3·39;	N : 11·79;	S : 16·00 %
Found:	C : 34·36;	H : 3·31;	N : 11·53;	S : ~15 %

Complex 130 : $[Fe(II)_2(H_2Los)(ClO_4)_2Cl(OH)]\cdot H_2O$

30 mL of dry EtOH was placed in a 3-necked flask and N_2 bubbled through as the solvent was brought to reflux. Solid $Fe(ClO_4)_2$ (4 mmol, 1·42 g) and 2 mmol of dfmp were added to the refluxing solvent and refluxed for 15 mins to form a deep blue solution. A fresh 2 mmol dahp solution was added dropwise to the refluxing mixture which was refluxed, under N_2 for 24 h during which time the volume had reduced to half. The volume was further reduced and the mixture set aside for slow evaporation. When it had almost evaporated to dryness a little dry EtOH was added and a black microcrystalline solid (complex **130**) was pipetted into a Hirsch funnel. On washing with 3 x 5 mL of dry EtOH this solid appeared to be a deep red-brown.

Yield : 0·11 g, 0·139 mmol, 14 %

IR : 3448, 1669, 1633, ~1605, 1534, 1091(spl), 626.

FAB-ms ($^m/_e$) : 1029·1(1), 945·1(1), 929·1(5), 687·0(8), 619(10), 586(20), 565·0(83), 481·0(26), 465·0(100).

Analysis for : $[Fe(II)_2(H_2$**Los**$)(ClO_4)_2Cl(OH)]\cdot H_2O$

Calculated :	C : 34·86;	H : 3·82;	N : 3·53;
Found :	C : 34·75;	H : 3·94;	N : 3·53;

Complex 131 : $[Fe_4LV5(ClO4)_4]\cdot 7H_2O\cdot CH_3OH$

50 mL of dry EtOH was placed in a 3-necked flask and N_2 bubbled through as the solvent was warmed. Solid $Fe(II)(ClO_4)_2$ (4 mmol, 1·46 g) was added and stirring commenced. A pale yellow solution formed and 2 mmol of solid dfmp was added to the refluxing solution which was refluxed for 15 mins. A 2 mmol dahp solution was added dropwise, from a pipette, to the refluxing mixture. The reaction mixture was refluxed, under N_2, for 22 h and allowed to cool to room temperature. After 2 days a brown powder was collected under vacuum.

Yield : 0·25 g, 0·197 mmol, 20 %

IR : 3420, 3175, 1662, 1628, 1557, 1086, 626.

FAB-ms ($^{m}/_{e}$) : 889·0(8), 753·0(15), 742·9(16), 717·0(8), 673·0(22), 636·0(52), 617·0(58), 600·1(100), 516·0(40).

The consistency of the analysis results (see below) indicates that the product is an homogenous mixture and that it must contain a lot of metal salt.

Analysis for :

Calculated :	C : ;	H : ;	N : %
Found :	C : ;	H : ;	N : %
	10·37	1·10	1·42
	10·54	1·16	1·40
	10·77	1·22	1·41

The filtrate of the above powder had been left under vacuum and had dried completely. Dry EtOH was added and it left to sit for 12 hours. A black crusty solid (complex **131**) was collected by vacuum filtration.

Yield : 0·24 g, 0·190 mmol, 19 %

IR : 3388, 3195, 1660, 1626, 1545, 1092, 625.

FAB-ms ($^{m}/_{e}$) : 956(3), 889(7), 824·0(3), 789(8), 773(7), 753·0(12), 708·0(12), 636·0(41), 600·0(62), 565·0(35), 516·0(26), 465·0(100)

Analysis for : $[Fe_4\mathbf{LV5}(ClO4)_4]\cdot 7H_2O\cdot CH_3OH$

Calculated :	C : 27·47;	H : 3·97;	N : 4·42;
Found :	C : 27·60;	H : 4·30;	N : 3·81;

CHAPTER 10

TOWARDS NEW LIGANDS

1 : INTRODUCTION

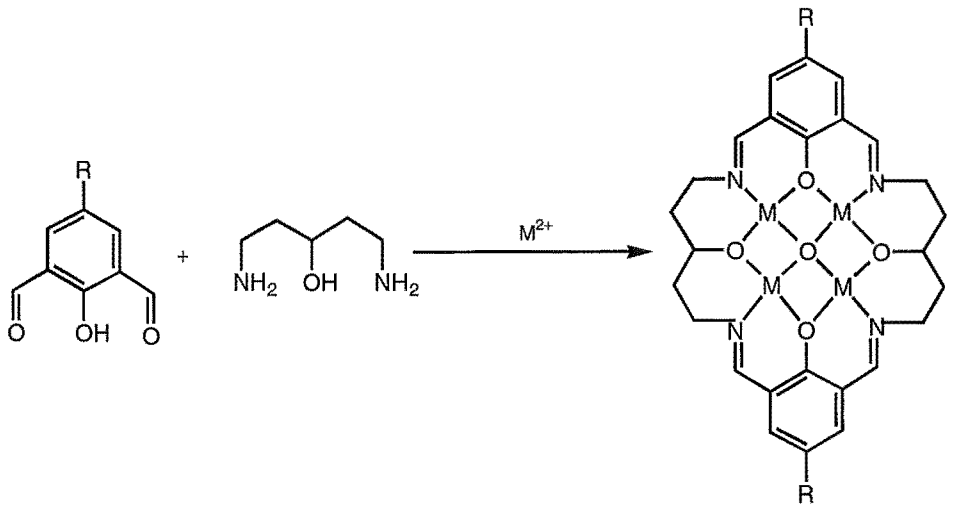


Figure 10·1

The [2 + 2] Schiff base condensation of 2,6-diformyl-4-methylphenol and 1,5-diaminopentan-3-ol had been successfully accomplished and tetranuclear complexes involving a range of metals (Fig. 10·1) had been synthesised. The tetranuclear macrocycles can dimerise, to form octanuclear species such as the copper complexes reported in Chapter 3, by coordination of the central oxygen species to a metal ion in an adjacent macrocycle. The macrocyclic core is a charged species as represented in Figure 10·2

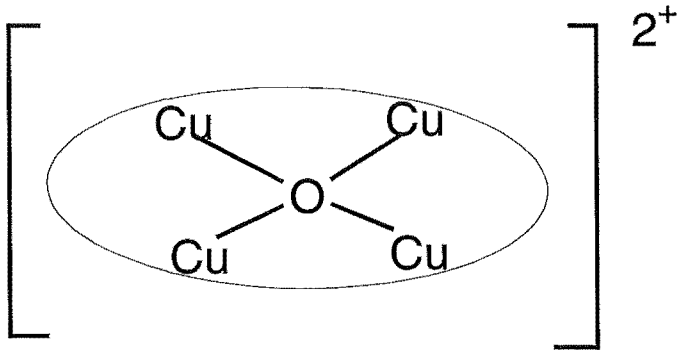


Figure 10·2

Modification of the macrocycle was proposed and two objectives were formulated.

The first objective was to change the functionalisation of the macrocycle to incorporate a charged substituent. As discussed in Chapter 3, tetranuclear complexes of this macrocyclic system dimerise by linking of the μ_4-O in the centre of one complex to a metal in a second complex. It was proposed that a charged substituent would give a neutral monomer which could form stacks, in the same manner as the dimerisation, to generate an extended array of macrocycles which can be envisaged along the lines of that shown in Figure 10·3. The SO_3^- group was chosen as the substituent.

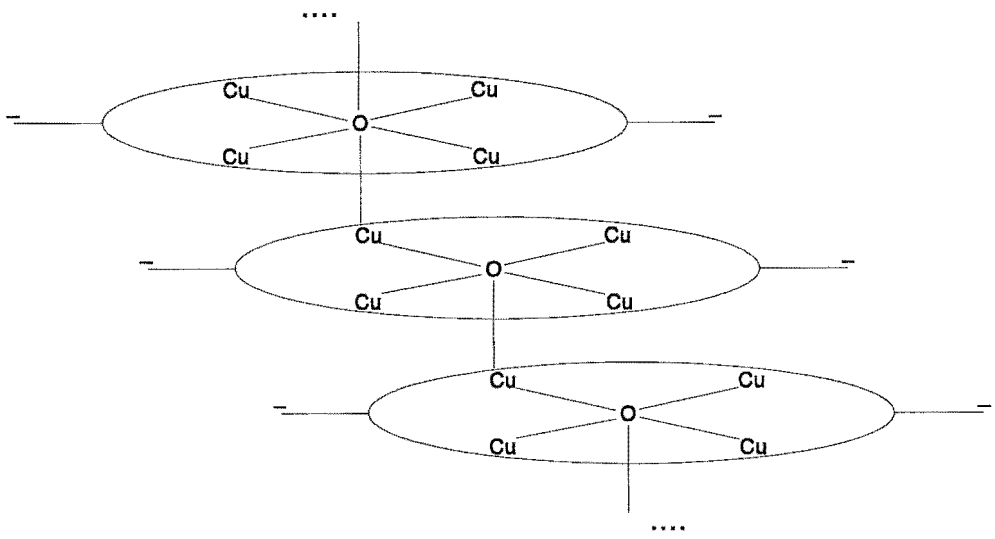


Figure 10·3

The second objective was to expand the macrocycle to allow the incorporation of more than four metals. The previous structural characterisation of planar tetranuclear copper complexes had demonstrated that the copper - oxygen distances in these complexes was reminiscent of those in metal oxides. It was thought that the binding of various groups to the copper ions in these arrays might lead to the development of corrosion control strategies and some work towards this was carried out in this project. A larger array would more closely model a metal surface.

1.1 : Development of 2,6-diformyl-4-sulfonylphenol

The Strategy

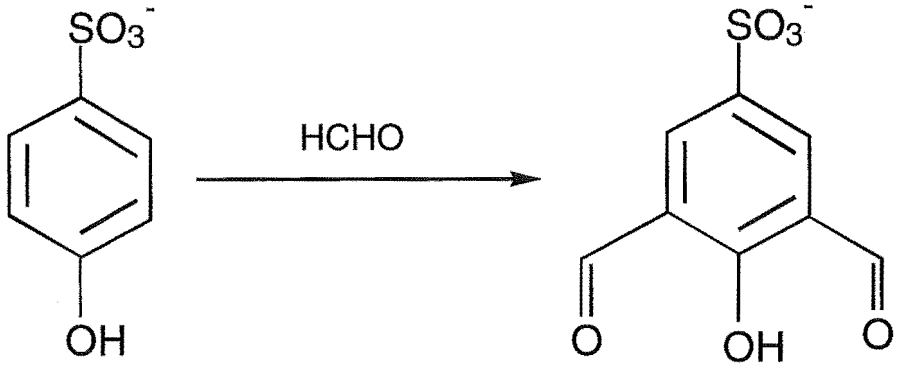


Figure 10·4

Sodium phenolsulfonate was chosen as the substrate for formylation as it is the sulfonated analogue of *p*-cresol; the starting material for the formation of dfmp. The conversion to 2,6-diformyl-4-sulfonylphenol (dfsp) was an adaption of the method used for the preparation of dfmp from *p*-cresol (Chapt. 2) In the dfmp synthesis p-cresol is formylated, the dihydroxy product precipitates from the aqueous reaction mixture and is tosylated before being oxidised, with dichromate, to the dialdehyde. It was anticipated that the sulfonated dihydroxymethyl product could be water soluble and therefore modifications of the rest of the synthesis could be necessary.

The Synthesis

Step 1 : Formylation of the phenol

The first step of the synthetic sequence was formylation. The sodium salt of phenolsulfonyl acid was added to a solution of NaOH and the very pale yellow solution was stirred for 30 mins. Formaldehyde was added and the mixture stirred 24 h. The progress of the reaction monitored by NMR; the signal for the hydrogens at 2 and 6 (6·85, 6·88 ppm) seen in the starting material (Fig. 10·5a) would be expected to disappear and they would be replaced by a signal for 7 and 8 (4·52 ppm) in the product (Fig. 10·5b).

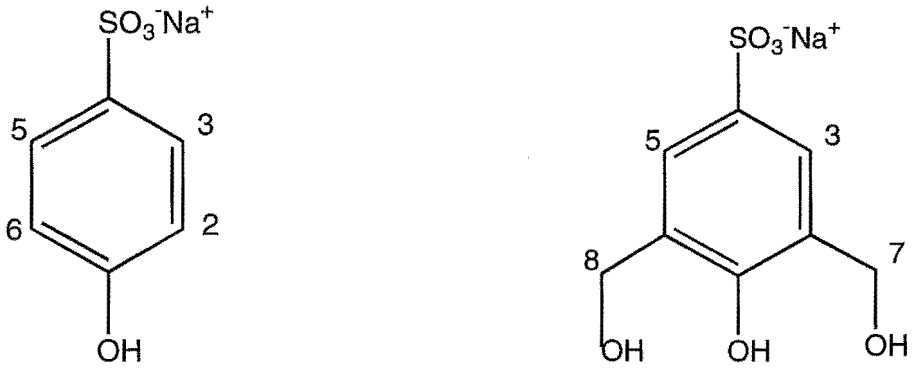


Figure 10·5

The first sampling, after 26 h stirring, showed ~10 % product had been formed. After 10 days more product had formed but as the reaction was progressing very slowly it was decided to heat the mixture to 50 - 60°C in an oil bath. The reaction was stirred at this temperature and sampling continued until the reaction appeared to have gone to completion; a total of 24 days (including ~ 14 days with heating). The reaction was tried again with refluxing and although this certainly sped up the formation of the desired product the reaction wasn't as clean so eventually this step of the reaction was carried out at ~60°C and under those conditions it goes to completion cleanly (in solution) in 8 days.

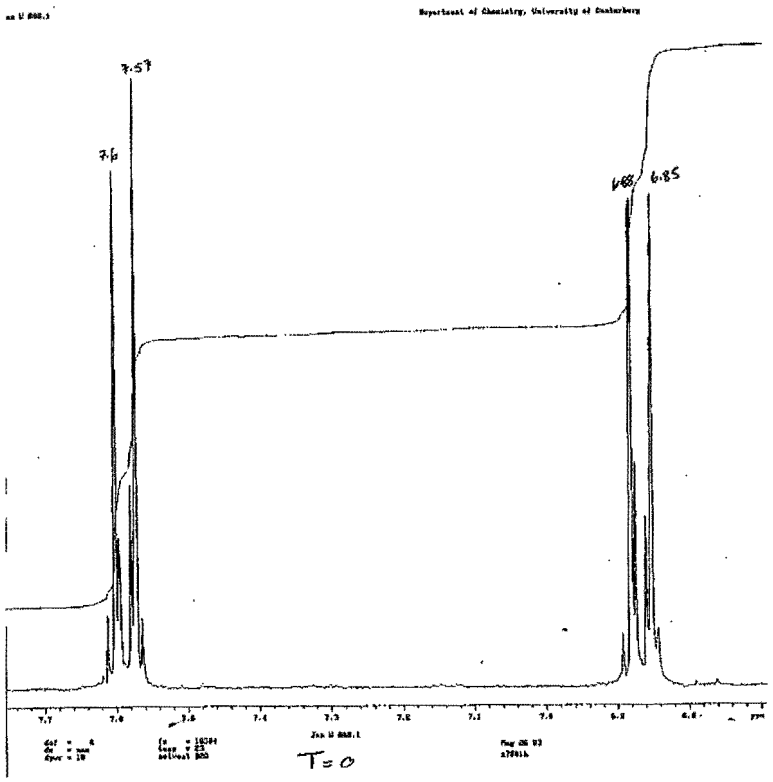


Figure 10·6a :
NMR Starting material H2,H6 - 6·85, 6·88 ppm and H3, H5 - 7·57, 7·9 ppm

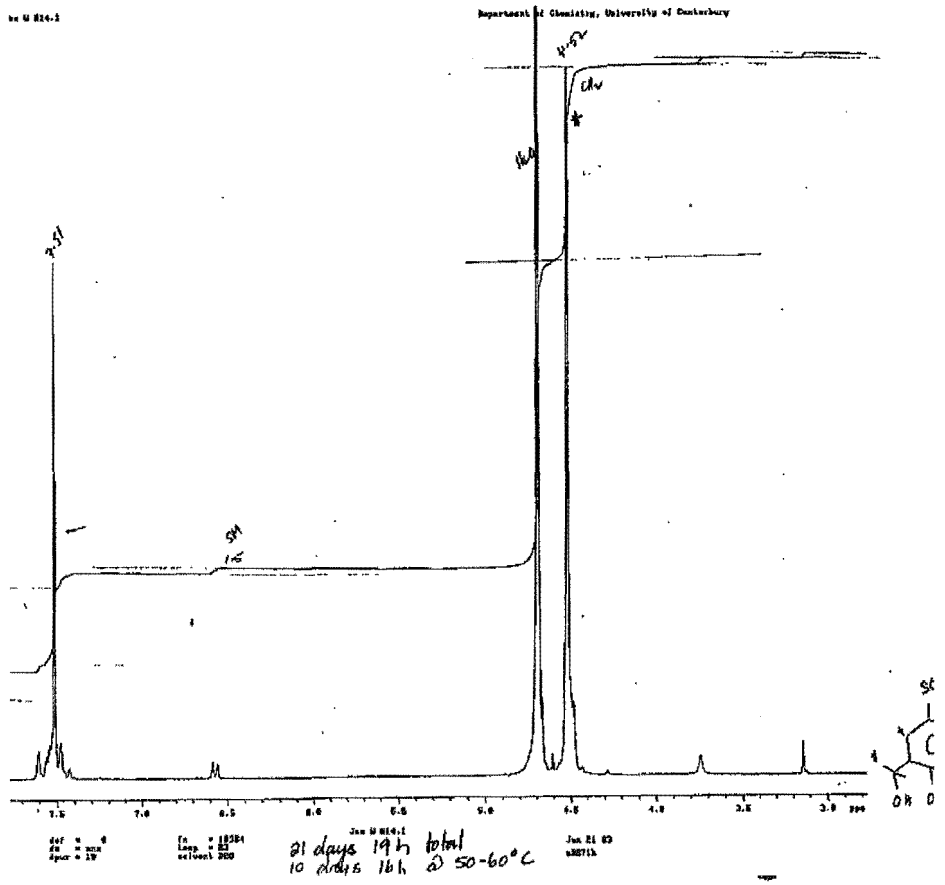


Figure 10·6a :
NMR Starting material Product H7,H8 - 4·52 ppm and H3, H5 - 7·51 ppm

Step 2 : Tosylation of the dialcohol

The dihydroxy product was made in solution and not isolated. It was necessary to adapt the tosylation as the tosylating agent, *p*-toluenesulfonyl chloride is not water soluble; it is freely soluble in alcohol, benzene and ether and soluble in toluene. A method of combining the aqueous phase containing the dialcohol and the organic phase containing the tosylating agent, would need to be developed. Two strategies were decided upon and both were be tested. The first was to dissolve the *p*-toluenesulfonyl-chloride in THF to form a mixed solvent system. The second was to dissolve the *p*-toluenesulfonyl chloride in toluene and to use a phase transfer catalyst (e.g. $Bu_4N^+X^-$) to carry the dihydroxymethyl product into the organic phase in the form shown in Figure 10·7.

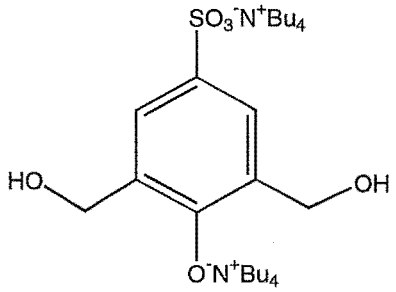


Figure 10·7 : The dsfp anion with phase transfer catalyst.

Both the proposed methods were tried. In the first a solution of *p*-toluene-sulfonyl chloride in THF was added to reaction solution containing the dialcohol and the reaction mixture was left stirring until NMR indicated that no starting material was left after ~ 7 days.

In the second method the phase transfer catalyst $Bu_4N^+I^-$ was stirred into the dialcohol solution and a hot solution of *p*-toluenesulfonyl chloride in toluene added to the stirring reaction mixture. After 5 days an NMR of a sample from the aqueous layer indicated the product was similar to that from the THF reaction. It was decided that the THF reaction was the better of the two as the product, in solution, was cleaner.

Experimentation with MnO_2 as an oxidising agent (refer Chapter 2) which was done subsequently to the synthesis just discussed, indicated that this would now be the oxidising agent of preference. Two advantages of MnO_2 are that protection of the phenol becomes unnecessary and that the desired dialdehyde is formed (at least for dfmp) in good yield.

A number of attempts were made to isolate the dialcohol from the reaction mixture before proceeding with the oxidation to a dialdehyde. A variety of extraction procedures was tried. An aliquot of the solution was taken and the pH adjusted to 5 by the addition of dilute HCl. At this pH it was expected that the phenol would be protonated and extraction of the product into an organic solvent might be possible. Extraction into $CHCl_3$ was tried and was unsuccesful. The remaining aqueous solution had more HCl added until a colour change, from the pale golden-yellow to an apricot colour, took place at pH ~ 3·5. A little more HCl was added to take the pH to 2. Extraction with

$CHCl_3$ produced a little solid. It was expected that the reaction mixture at pH 2 should have contained product, maybe some formaldehyde and NaCl. The aqueous solution was reduced under vacuum to dryness and mixed with MeOH. It was expected that any remaining formaldehyde would come off under vacuum and that the product might (like its $-CH_3$ analogue) dissolve in the MeOH leaving any NaCl behind. The EI-ms of the solid from this treatment showed that the desired product was indeed present but the chemical analysis indicated that it was still contaminated with NaCl. The MeOH solution was again dried and the solid variously treated with $CHCl_3$, toluene and propan-2-ol without much product being collected from any of these treatments.

A second aliquot of the reconstituted solution was extracted with CH_2Cl_2 with no success. The remaining aqueous portion had the pH adjusted to 2, was dried to a solid and stirred and heated in IPA. This treatment had been decided upon as it seemed likely that not all of the water be removed from the product when drying under vaccum and that any remaining water was probably carrying the NaCl into the MeOH solution and this was not expected to happen with IPA. A small amount of product was collected from this treatment.

A third aliquot was taken and the pH adjusted to 1. This solution had the water removed under vacuum. MeOH was added and the solvent removed under vacuum twice more. The remaining solid was then extracted, using IPA in a soxhlet apparatus, over a period of three days. During this time the solvent became a golden colour and some creamy coloured solid appeared in it. When the solvent was removed under vacuum a golden brown sludge remained. As this smelled very strongly of IPA dry MeOH was added and the solvent removed again. The resulting product was a pink-brown material of a toffee consistency. Chemical analysis and EI-ms indicated that the desired dialcohol had been extracted.

The dialcohol had $CHCl_3$ added and was treated *in situ* with activated MnO_2. After three days the product was separated from this mixture as a dark brown oil which eventually solidified to a pink-brown solid. Microanalysis and FAB-ms indicated that the desired dialdehyde had been achieved.

A template synthesis using this material with cobalt perchlorate and dahp yielded a pale green powder and a darker green granular material. The IR indicates that a macrocyclic product has been formed. This has not yet been fully characterised.

2 : TOWARDS A SIX METAL PLANAR ARRAY

A planar macrocyclic complex incorporating more than four metals held by oxygen donors would more closely model a metal surface than the tetranuclear complexes already achieved. Although Robson has developed interesting macrocyclic complexes incorporating six metals* none of these is planar. However while the work in this project was in progress, hexanuclear planar complexes were reported. Tandon has synthesised a number of planar six copper complexes by the [3 + 3] condensation of dfmp and 1,3-diaminopropan-2-ol.[49,237]

Lingga[204d] has synthesised two hexanuclear complexes of a ligand formed by the [3 + 2] Schiff-base condensation of 1,3-diamino-2-propanol with 4- *t*-butyl-2,6-diformylphenol. The cation of $[Cu_6\mathbf{M25}(\mu\text{-}OH)_4]^{3+}$ is shown in Figure 10·8. The least-squares planes through the two phenol rings of **M25** are inclined at 2° to each other; the cation has an almost planar conformation.

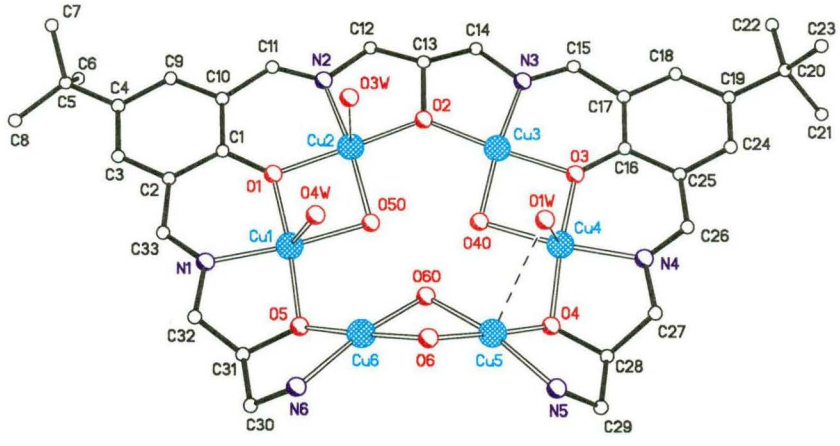


Fig. 10·8 : A perspective view of the hexacopper(II) cation $[Cu_6M25(\mu\text{-}OH)_4]^{3+}$ of complex M25, shown with the atom numbering system.

* These have been discussed in detail in Chapter 1.

It was considered that an expansion of the **LV5** system could achieve the desired planarity. The two design strategies (Fig. 10·9) to achieve this expansion were to extend either the diamino lateral chain or the head unit and incorporate additional oxygen functions.

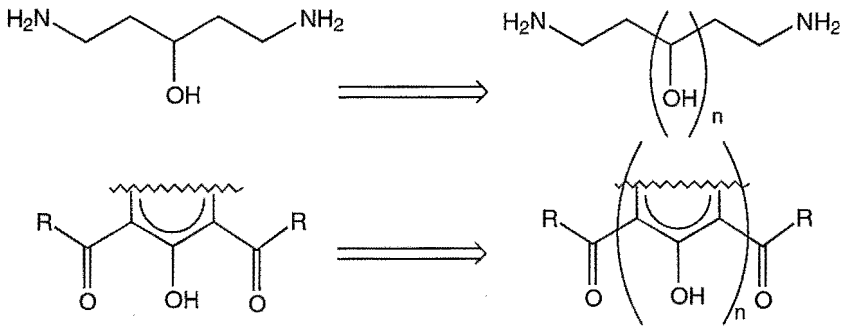
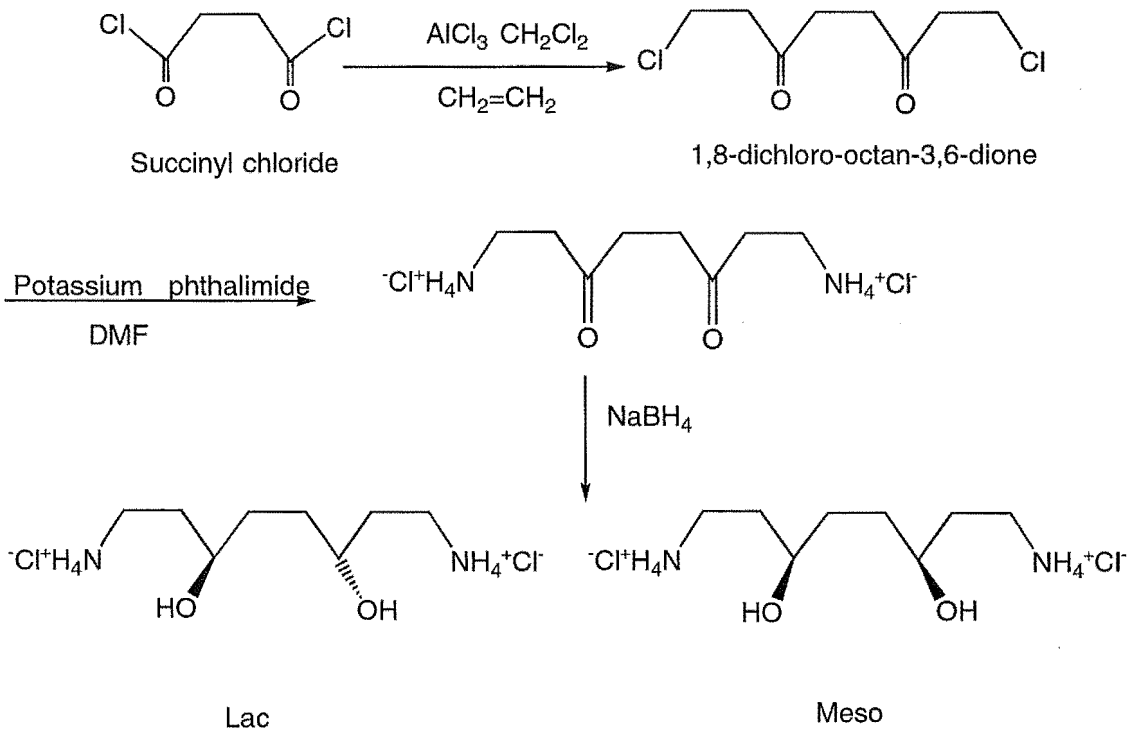


Figure 10·9

2·2 : Extension of the Diaminoalcochol.

The general strategy for this synthesis, as outlined below (Scheme 1), was an adaptation of that used to prepare 1,5-diaminopentan-3-ol from propanoyl chloride (Chapt. 2).



Scheme 1 : The synthetic strategy for 1,8-Diamino-octan-3,6-diol

The preparation of 1,5-diaminopentan-3-ol preparation was effected by the Friedel Crafts alkylation of propanoyl chloride. For the proposed synthesis, succinyl chloride was chosen as the starting material as it had two groups to which it was hoped carbons would be added. The product was collected as a brown-black viscous oil. NMR spectroscopy indicated the desired dichloride was present and the material was reacted with phthalimide without further purification. The NMR of the phthalimide product indicated that it contained the desired diphthalimide mixed with other unidentifiable products. Repetition of the reaction on different scales failed to generate the pure diphthalimide. In view of the complex mixtures of materials produced coming from the presence of double functionalities, this approach was not pursued further. It is now considered that chromatography could be employed to separate these products and this will be further investigated.

2·3 : Extension of the Head Unit

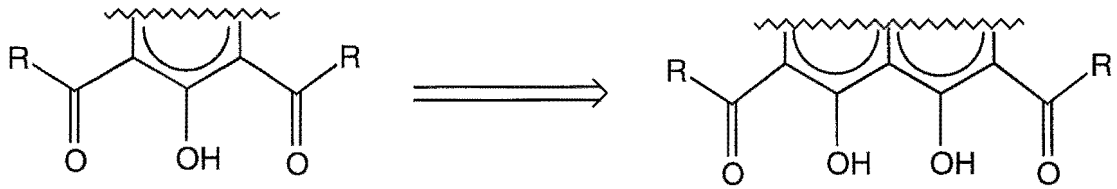


Figure 10·10

Extension of the head-unit was envisioned in the manner illustrated in Figure 10·10. Ideally the carbonyl functionality would be an aldehyde rather than a ketone for the reasons discussed previously. 2,7-Diformyl-naphthalene-1,8-diol would be a good head unit to react with 1,5-diaminopentan-3-ol as it had both the appropriate donor groups and was of a rigid nature. The rigidity is needed to promote planarity in any resulting complex. A literature search showed that 2,7-diformyl-naphthalene-1,8-diol had never been made but a preparation for 2,7-diacetyl-1,8-dihydroxy-3,6-dimethyl-naphthalene (H_2daddn) (Fig. 10·11) had been reported.[238, 239]

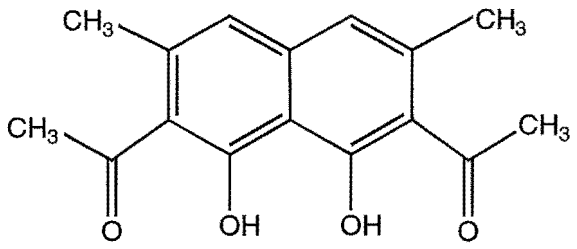


Figure 10·11 : H_2daddn

Robson's group had been able to form a macrocyclic ligand (Figure 10·12) by reacting H_2daddn with ethylene diamine (en).[239] Efforts to form binuclear macrocyclic complexes of this ligand either by using the preformed ligand or by template procedures were unsuccessful. Neither Cu(II) nor Pd(II) was able to be inserted into the preformed macrocycle.

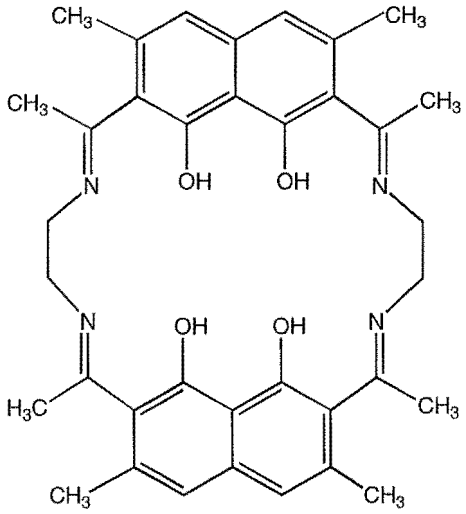


Figure 10·12 : Ligand formed between H_2daddn and En

However a palladium complex (**M26**) formed (Fig. 10·15), when an attempt was made to make a binuclear podal complex of the type shown in Figure 10·13, indicates a reason for the template procedure being unsuccessful.

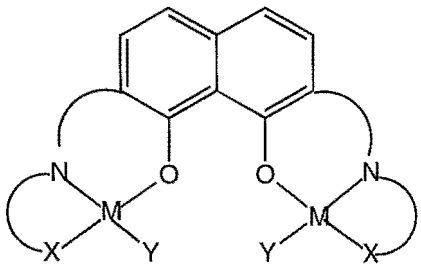


Figure 10·13 : Desired podal complex

NMR spectroscopy confirmed that reactions between either 2-(aminomethyl)-pyridine or 2-(aminoethyl)-pyridine with H_2daddn resulted in only mono-Schiff base formation and not the hoped for di-Schiff bases ligands under any conditions. The results were the same when metal ions were used to promote di-Schiff base formation and Figure 10·14 shows the types of products isolated from these reactions.

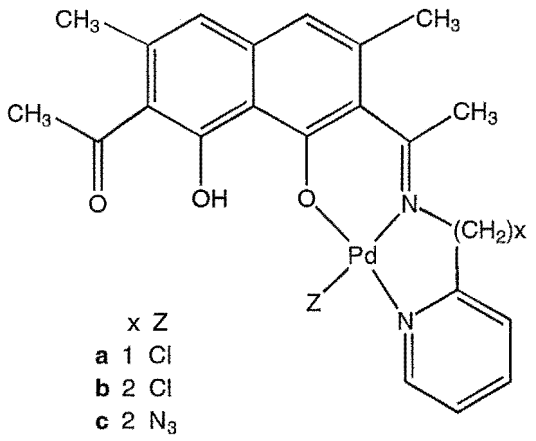


Figure 10·14

Figure 10·15 shows the mono-Schiff base palladium azide complex (**M26**) isolated from one reaction. The macrocycle exhibited a marked fold that resulted in the average metal coordination plane being inclined at 54·5° to the average naphthalene plane. Robson suggested that steric repulsion between the methyl groups at C9 and C12 would be extreme if the imine were coplanar with the naphthalene and that this was most likely responsible for this fold. The acetyl group which had failed to form a Schiff base was twisted around the C18 - C19 bond in such a way that the C20 - C19 - O3 plane was almost perpendicular to the naphthalene unit. It was considered that repulsion from the adjacent methyl group C17 was the most probable cause of this twisting. This configuration inhibits the formation of the second imine link.

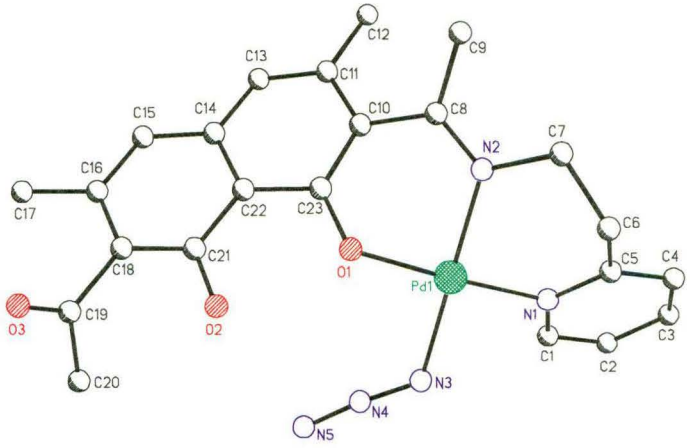
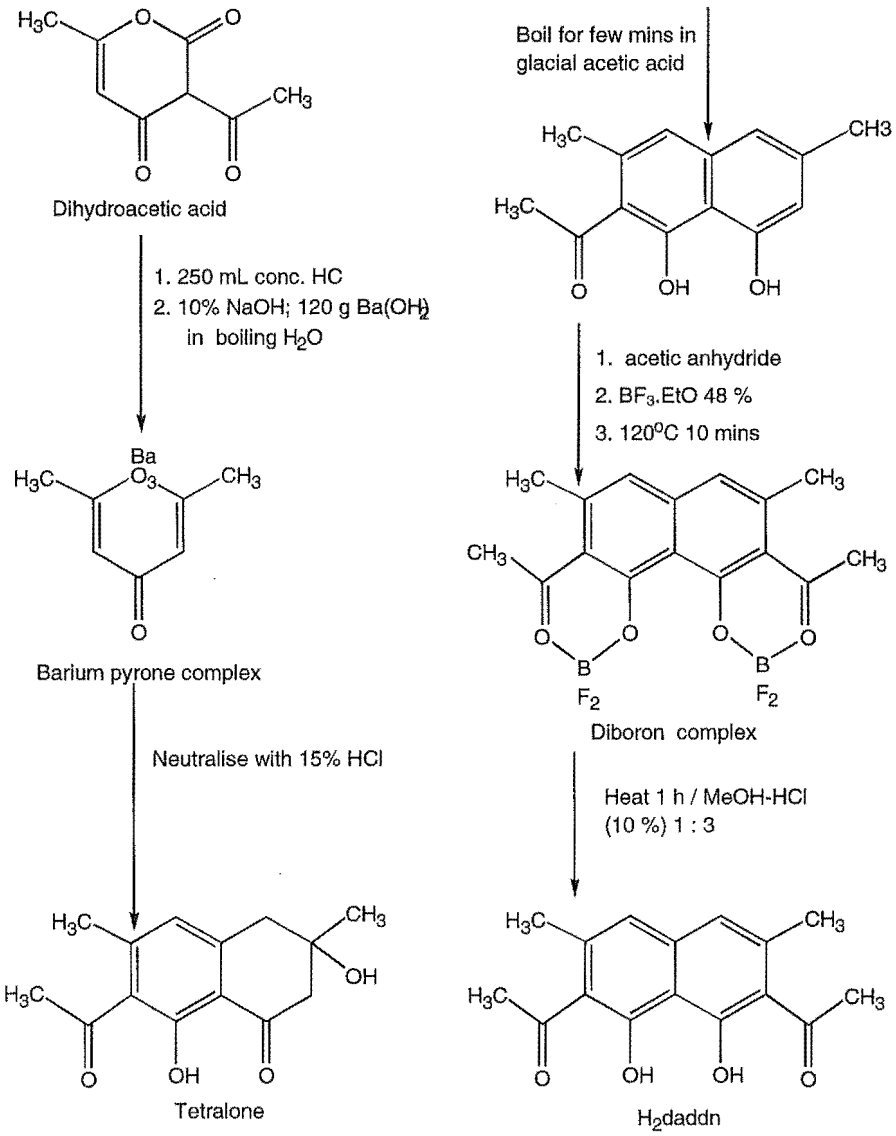


Figure 10·15 : The mono-Schiff base palladium azide complex of H_2daddn

The use of H_2daddn and 1,5-diaminopentan-3-ol offered the possibility for the formation of many interesting complexes. It was anticipated that incorporation of metals into any [2 + 2] macrocycle formed from these moieties could be hampered by interaction of the acetyl methyl groups with the methyl substituents on the naphthalene in the same way as in the Robson complexes but it was decided that any products would be of interest. It was hoped that the longer chain and the flexibility of 1,5-diaminopentan-3-ol over ethylenediamine might facilitate [2 + 2] macrocycle formation.

2·3·1 : Preparation of H_2daddn

H_2daddn was prepared by Robson's[239] improvement of the method of Casabo.[238] This is a difficult synthesis and proceeds by the steps outlined in Scheme 2. The first step is the formation of barium dimethylpyrone from dihydroacetic acid. Dihydroacetic acid formed a very thick creamy suspension with concentrated HCl and the mixture boiled until only a deep yellow solution remained. The solution was reduced under vacuum at 50 - 60°C to leave a semi-solid yellow mass which solidified on cooling. The residue was dissolved in NaOH solution to form a golden brown solution which was mixed with a solution of barium hydroxide. A fine precipitate formed at once and the mixture was left to cool. The barium dimethyl pyrone was collected, as yellow powder, in a frit and dried under vacuum.



Scheme 10·2 : The preparation of H_2daddn

The next step was to convert this pyrone to 7-acetyl-3,8-dihydroxy-3,6-dimethyl-1-tetralone. The yellow solid was made into a paste with water and 15% HCl added until the solution was neutral and almost all of the solid was dissolved. The solid which formed at this point was collected by filtration. If clean tetralone is recovered at this point conversion to 2-acetyl-3,6-dimethylnaphthalene-1,8-diol (H_2addn) is achieved by boiling it for a few moments in the acetic acid.

Difficulties were experienced in isolating clean tetralone. However, subsequent investigation of this step of the procedure indicated that if all solids formed at

this point are refluxed for an hour in glacial acetic acid H_2addn precipitates out of the filtered solution as soon as it starts to cool.

The conversion of H_2addn to H_2daddn is achieved by the formation of a diboron complex. H_2addn was taken in acetic anhydride and $BF_3{\cdot}Et_2O$ was added. This mixture formed a bright red solution on heating to 120°C. The solution was stirred at this temperature for 10 mins by which time a yellow precipitate was forming. On cooling these yellow crystals were collected and shown (by IR, MS, and chemical analysis) to be the required diboron complex. The identifying ν(C = O) of Daddn$(BF_2)_2$ appearing at 1610 cm^{-1} was seen; in derivatives with one or both acetyl groups uncoordinated ν(C = O) appears at 1695 - 1660 cm^{-1}.

The Daddn$(BF_2)_2$ was converted to H_2daddn almost quantitatively by suspending it in a mixture of 10 mL of MeOH and 3 mL HCl(10%) and refluxing for ~1 h. The solid, now a lemon-yellow colour, was collected in a frit and washed with MeOH until all residual golden-yellow colour was removed. Although the overall yield of this reaction was less than 1 % the synthesis of H_2daddn was achieved.

A second synthesis incorporating a further modification by Robson[240] was tried. The dihydroacetic acid was dissolved in boiling concentrated HCl over one hour. The water was removed under vacuum and the resulting creamy-yellow solid was dissolved NaOH solution to form a golden solution. Solid $Ba(OH)_2$ was added to the heated solution and the mixture was brought to the boil with stirring. This modification inhibits the formation of $BaCO_3$. The colour changed from creamy-yellow to lemon-yellow and a fine precipitate formed as the barium hydroxide dissolved. The mixture was boiled for a few minutes, left to cool and two hours later the yellow precipitate filtered off.

HCl solution was added to this solid in a beaker and the undissolved $BaCl_2$ removed by filtration. The resulting solution was extracted with CH_2Cl_2 and the solvent removed under vacuum to produce a golden brown oil. Piperidine was added to this oil as it was heated on a steam bath. The mixture went brown and tarry but didn't solidify, the product was dissolved in glacial acetic acid and

boiled for a few minutes after which the dark brown solution set aside to cool. After one week the crusty yellow solid which had formed was collected. The total yield of H_2addn in this preparation was 3·91 % compared to 15·48 % in the first preparation.

2·3·2 : Ligand Elaboration

It was decide to try and form a free ligand before attempting a metal template reaction. The procedure developed by Robson for the ligand shown in Figure 10·4 was followed. The H_2daddn suspension in MeOH was stirred in a round-bottom flask while the dahp solution was added through a filter paper and the resulting mixture refluxed for 24 h. The H_2daddn gradually dissolved over the first three hours of refluxing and the colour of the reaction solution changed from lemon yellow to a deep orange gold over that time. As the reaction mixture cooled a fine yellow powder precipitated out. Tiny crystals were isolated but they were unsuitable for X-ray analysis. Over time the colour of the powder changed from the original yellow through an orangey-brown to a very dark khaki colour. No parent ion could be seen in the EI-ms and the product's intractable insolubility made NMR impossible. Chemical analysis indicated that the macrocycle had not formed and the product was not homogenous.

3 : CONCLUSIONS AND FUTURE WORK

$-SO_3R$ $-CO_2R$ $-OH$

The above moieties are being considered as charged substituents on the phenol. 2,6-diformyl-4-hydroxyphenol is known and has been used to form binuclear podand copper complexes[121]. The synthesis of a phenol bearing a charged substituent may be approached by using a group that masks the anion. Both sulfonated or carboxylated phenols could be accessible through this route. A synthesis for esters of the carboxylated phenol has been found.[241]

The extended macrocycle is most likely to be achieved with a formylated head unit and two approaches to its formation can be made. The first is to modify the

acetyl group of H_2daddn to form a dialdehyde. The second would be to formylate naphthalene-1,8-diol.

EXPERIMENTAL

1 : SYNTHESIS OF 2,6-DIFORMYL-4-SULFONYLPHENOL

1·1 : The First Synthesis

Step 1 : Formylation of the phenol

Phenolsulfonyl acid sodium salt (107·085 g, 0·5 mol) was added to a solution of NaOH (32 g, 0·8 mol) in H_2O (100 mL) in a 500 mL round bottomed flask. As all the salt had not dissolved after stirring some time a further 50 mL of H_2O was added. The very pale yellow solution was stirred 30 mins. Formaldehyde (37 %, 1·325 mol, 107·5 g, 116·42 mL) was added and the mixture stirred. After 10 days the mixture was heated to 50 - 60°C in an oil bath. The reaction was stirred at this temperature and sampling continued until it appeared to have gone to completion; a total of 24 days (including ~ 14 days with heating).

Step 2 : Tosylation

Method 1 : Using the tosylating agent in THF

The dialcohol solution (225 mL, 0·25 mol) was stirred in a round bottom flask. *p*-Toluenesulfonyl chloride (61·75 g, 0·325 mol, [1·3 : 1 to dialcohol]) dissolved readily in THF (100 mL). The resulting pale yellow solution was added to the golden reaction mixture which became cloudy and developed a pinkish-brown colour. This quickly cleared to a pink solution which faded through an orangey-brown to a clear pale yellow. The reaction mixture was left stirring until NMR indicated that no starting material was left in ~ 7 days.

Method 2 : Using toluene and phase transfer catalyst.

The dialcohol solution (225 mL, 0·25 mol) was stirred in a round bottom flask. The phase transfer catalyst $Bu_4N^+I^-$ was stirred into this solution and most of it dissolved. *p*-Toluenesulfonyl chloride (61·75 g, 0·325 mol, [1·3 : 1 to dialcohol]) was heated in toluene (100 mL) until it dissolved and added hot (to prevent precipitation of *p*-toluenesulfonyl chloride) to the stirring reaction mixture. The toluene phase instantly went brown and formed a layer on top of the aqueous

phase but within 20 mins had dispersed through the aqueous material. After 4 days stirring NMR indicated that the reaction was completed. The reaction mixture was now a brown emulsion with some dark crystalline material adhering to the flask walls. After sitting 36 h the reaction mixture was a deep brown toluene layer with a golden brown aqueous layer underneath. An NMR of a sample from the aqueous layer indicated the product was similar to that from the THF reaction.

As a result of this investigation it was decided to start with a new preparation, to do the first step with gentle heating, and to isolate the product at the end of the first step before attempting the oxidation.

1·2 : The Second Synthesis

Step 1 : Phenolsulfonyl acid sodium salt (107·09 g, 0·5 mol) was added to a solution of NaOH (32 g, 0·8 mol) in distilled H_2O (150 mL) in a 500 mL round bottomed flask. The very pale yellow solution was maintained at ~60°C (56 - 64) and stirred 30 mins. Formaldehyde (37 %, 120 mL) was added and the mixture stirred until NMR indicated that the reaction had gone to completion in 8 days.

Separation of a small sample of the product as the barium salt of the sulfonate group was not successful.

A 250 mL aliquot was taken and the pH adjusted to 1 and the water removed under vacuum. MeOH was added and the solvent removed under vaccum twice more. The remaining solid was then extracted, using IPA in a soxhlet apparatus, over a period of three days. During this time the solvent became a golden colour and some creamy coloured solid appeared in it. When the solvent was removed under vacuum a golden brown sludge remained. As this smelled very strongly of IPA dry MeOH was added and the solvent removed again. The resulting product was a pink-brown material of a toffee consistency.
Yield : ~3 g, 18·5 mmol.

Analysis for : $C_8H_9O_6SNa·2·5(CH_3OH)$

Calculated :	C : 37·50;	H : 5·68 %
Found :	C : 37·68;	H : 5·69 %

Step 2 : Oxidation of the dialcohol

The dialcohol was left in the round bottomed flask an $CHCl_3$ added with 25g of activated MnO_2. This mixture was stirred at RT for 3 days after which time it was filtered and MnO_2 washed with MeOH 3 times. The resulting golden yellow solution was reduced under vacuum to form a brown oil which eventually dried to a pink-brown solid.

Yield : 0·285 g, 13·93 mmol, 75·3 % (of the above dialcohol).

1·4 : Formation of a disulphonated macrocycle

All of the diformyl sulfonated phenol (dfsp) was used to make a cobalt macrocycle. Dsfp (2·285 g, 9·756 mmol) was dissolved in dry MeOH to form a golden solution. Two metal equivalents of $Co(ClO_4)_2$ (3·615 g, 9·756 mmol) was dissolved in MeOH and added to the dsfp to form a brownish moss green solution. Two metal equivalents were used because there was not enough $Co(ClO_4)_2$ left to use four. The mixture was refluxed for 10 mins. and then dahp solution added. The reaction mixture was refluxed for 60 h after which time the product, a mixture of a dark green granular solid and some pale green powder was filtered off.

Yield : 0·972 g, 0·963 mmol, 21·98 %

IR : 1631, 1577, triplet 1153, 1116, 1083, 627 - very interesting in OH and NH_2 region - maybe some free amine.

The sample, microanalysis and FAB-ms results were lost between Belfast and Christchurch.

2 : PREPARATION OF 2,7-DIACETYL-1,8-DIHYDROXY-3,6-DI-METHYL-NAPHTHALENE (H_2daddn)

2,7-diacetyl-1,8-dihydroxy-3,6-dimethylnaphthalene (H_2Daddn) was prepared by Robson's[239] improvement of the method of Casabo[238]

Step 1 : Formation of Barium dimethylpyrone.

Dehydroacetic acid (50g, 0·297 mol) formed a very thick creamy suspension with concentrated HCl (260 mL) and the mixture boiled until a deep yellow solution formed. This was reduced under vacuum at 50 - 60°C to leave a semi-

solid yellow mass which solidified on cooling. This residue was dissolved in 10% NaOH solution (125mL) to form a golden brown solution. This was to be mixed with a $Ba(OH)_2$ in water but each time they were mixed, the solution quickly became contaminated with $Ba(CO_3)_2$. To overcome this 200 mL of water was brought to the boil, the 120g of $Ba(OH)_2$ added, stirred for a few seconds and quickly added to the reaction solution through a filter paper. A fine precipitate formed at once and the mixture was left to cool. The barium dimethyl pyrone was collected, as yellow powder, in a frit and dried under vacuum. Yield : 113·2 g, 0·283 mol, 95 %.

Step 2 : Formation of 7-acetyl-3,8-dihydoxy-3,6-dimethyl-1-tetralone.

The barium dimethyl pyrone (113·2g) was made into a paste with water and 15% HCl added. At ~pH 7 the mixture was filtered. The solid was made into a slurry with water (150 mL) and glacial acetic acid (5 mL) added. The mixture was brought to 70°C, filtered and the filtrate set aside. After 6 days solid had appeared in this solution and was collected (0·381g). m.p. - 110° (Lit 137 - 138°) showed that it was not the tetralone product. The original brown filtrate had been set aside too and now contained some solid. This also was not clean tetralone.

Step 3 : Formation of 2-acetyl-3,6-dimethylnaphthalene-1,8-diol (H_2addn).

All of the solids formed in the last step (a mixture of yellow "fluffy" crystalline material and much more of a dark yellow solid crusty material (10.23g)) were combined and refluxed in glacial acetic acid for 3 h (all dissolved). A crystalline product started to form in the orange-gold solution as soon as refluxed was stopped. These crystals (bright lemon-yellow needles) were collected by vacuum filtration.

Yield : 5·372 g, 0·023 mol, 15·48 % (of dihydroxyacetic acid).

m.p. 181 - 183° (Lit : 182 - 184°)

I. R. - Lit. :ν_{Max} (Nujol) : 3270, 1636s, 1600(sh), 1583s cm^{-1}

Found : 1637, 1599, 1582

Analysis : for $C_{14}H_{14}O_3$)

Calculated : C : 73·03; H : 6·08 %

Found : C : 72·62; H : 6·02 %

Step 4 : Conversion of H_2addn to H_2daddn.

H_2addn (2·96g, 12·9 mmol) was suspended in 12 mL of acetic anhydride. BF_3·Et_2O (48%, 6·55mL, 52 mmol) was added. On addition of BF_3·Et_2O a red colour appeared and then everything dissolved to form a deep orangey-brown solution. The temperature was maintained between 120 and 130°C and within 10 mins a yellow precipitate was forming in the solution. The mixture was refluxed for a further 10 mins and left to cool.

Yield : 2·49 g, 7·0 mmol, 54 % (Lit. 54%)

m.p. : 184 - 194°C (decomposed) Lit : 192 - 194°C

Analysis; for $C_{16}H_{14}B_2F_4O_4$:

Calculated : C - 52·20, H - 3·80 %

Found : C - 52·26, H - 3·61 %

I. R. : Literature : Daddn$(BF_2)_2$ν(C = O) - 1610 cm^{-1}

Found : 1610 cm^{-1}

Literature EI-ms ($^m/_e$)(15eV) :

348(M - F, 5), 328(M - 2F,5) 300(100), 285(43), 258(34), 243(14), 216(40 %)

Found (70 eV) 300 285 258 243 214

Daddn$(BF_3)_2$ (0·295 g, 0·8 mmol) was added to 10 mL of MeOH and 3 mL HCl and refluxed ~1 h. The solid, now a lemon-yellow colour, was collected in a frit and washed with MeOH until all residual golden-yellow colour was removed.

Yield : 0·197 g, 0·72 mol, 90·1 % (Lit. : Almost quantitative)

Analysis : for $C_{16}H_{16}O_4$

Calculated : C : 70·60, H : 5·75 %

Found : C : 70·35, H : 5·75 %

I. R. : Found ν(C = O) : 1684 and 1628 cm^{-1}

EI-ms ($^m/_e$) (70eV) Lit : 272 (M^+, 85), 257(100), 239(95), 115(10), 43(22 %).

EI-ms ($^m/_e$) (70eV) Found : 272 (M^+, 87), 257(100), 239(97), 115(11), 43(%)

Overall yield : 15·48 %.

2 : THE SECOND PREPARATION OF H_2daddn

Formation of 2-acetyl-3,6-dimethylnaphthalene-1,8-diol (H_2addn).

Dehydroacetic acid (14·03 g, 0·083 mol) was suspended in hot concentrated HCl (130 mL) and boiled until it all dissolved (1 h). The water was removed under vacuum at 50 - 60°C to form a creamy-yellow solid. The residue was dissolved in 40 mL of 10% NaOH solution to form a golden solution. Solid $Ba(OH)_2$ (33·74g, 0·107 mol) was added to the hot solution and the mixture was brought to the boil with stirring. The colour changed from creamy-yellow to lemon-yellow and a fine precipitate formed as the barium hydroxide dissolved. The mixture was boiled for a few minutes, left to cool and 2 h later the yellow precipitate filtered off.

15% HCl solution (~75 mL) was added to this solid in a beaker and the $BaCl_2$ removed by filtration. The resulting solution was extracted with 4 x 30 mL aliquots of CH_2Cl_2 and the solvent removed under vacuum to produce a golden brown oil. Piperidine (0·631g, 0·5 mL (5 drops)) was added to this oil and it was heated on a steam bath for 35 mins. The mixture went brown and tarry but didn't solidify. The mixture was dissolved in 40 mL glacial acetic acid and boiled for a few minutes and the dark brown solution set aside to cool. After 1 day a few fine yellow crystals had appeared in this solution and after 1 week the crusty yellow solid which had formed was collected in a frit.

Yield : 0·112 g, 0·487 mmol, 1·2 %

m.p. : 183·1 - 183·3°C (Lit : 182 - 184°C)

I. R. : Lit. :ν_{Max} (Nujol) : 3270, 1636s, 1600(sh), 1583s cm^{-1}

Found : 1637, 1598, 1582 cm^{-1}

Analysis : for $C_{14}H_{14}O_3$

Calculated : C : 73.03, H : 6.08 %

Found : C : 72.68, H : 6.16 %

After two weeks the filtrate had some crusty brownish-yellow solid in it . This was boiled in glacial acetic acid. After 2 h a bright yellow solid had formed. The solid was collected in filter paper and the golden-brown filtrate set aside.

The solid became white after a while and was discarded. After 10 days the filtrate contained yellow crystalline material which was collected in a frit.

Yield : 0·262 g, 1·14 mmol, 2·74 %

m.p. : 179·9 - 180·8°C (Lit : 182 - 184°C)

I. R. : not very good but appropriate peaks just discernible

Analysis : for $C_{14}H_{14}O_3$:

Calculated : C : 73·03, H : 6·08 %

Found : C : 71·38, H : 6·03 %

The total yield of H_2addn in this preparation was 3·91 %. As 15·48 % was recovered in the first preparation it appeared that it had been more successful.

Preparation of the Diboron complex

The combined H_2addn (2·079 g, 9·03 mmol) was added to 8·3 mL of acetic anhydride and the suspension heated on an oil bath at 130°C. BF_3EtO (4·6 mL) was added and the residual solid dissolved to form an orangey-red (rather than the expected bright red) solution formed. The mixture was stirred at 115 - 130°C for 15 mins. , The product was collected after the RM had cooled.

m.p. : 189·3 - 191·3°C (Lit : 192 - 194°C)

Analysis : for $C_{16}H_{14}B_2F_4O_4$:

Calculated : C : 52·20, H : 3·80 %

Found : C : 71·06, H : 5·92 %

A subsequent mass spectrum showed that the diboron complex had not formed and the synthesis was not proceeded with.

2·3·2 : Synthesis of a Complex with H_2daddn.

The procedure developed by Robson[239] was followed. DahpCl_2 (0·0917 g, 0·48 mmol) was dissolved in 3 mL dry MeOH and KOH (0·96 mmol, 4·8 mL (previously prepared solution)) was added. The solution was sat in ice to precipitate the maximum KCl. H_2daddn (0·103 g, 0·38 mmol) was suspended MeOH (3 mL) in a 25 mL round-bottom flask. The dahp solution was added, through a filter paper, to the stirring H_2daddn suspension and the resulting mixture refluxed for 24 h. The H_2daddn gradually dissolved over the first 3 h of refluxing and the colour of the reaction solution changed from lemon yellow to a deep orange gold over that time. As the reaction mixture cooled a fine yellow powder precipitated out. The flask was left for 3 days by which time the the walls were now also coated with fine powder product and all of the product had changed to a more orangey colour. After a further two days this product was now orange brown with some tiny crystals apparent in a brown solvent. For this reason it was decided to leave the mixture, covered with parafilm, for more time in hope that crystals big enough for X-ray analysis may be achieved. After a week it appeared that no more product had formed but the powder was now a very dark khaki colour. It was collected by vacuum filtration and the filtrate was a reddish brown.

Yield : 0·075 g, 0·111 mmol

Analysis for : $C_{38}H_{42}O_6N_4$

Calculated :	C : 70·13;	H : 6·51;	N : 8·61%
Found :	C :;	H : ;	N : %
	59·75	**5·64**	**5·76**
	58·79	**5·42**	**5·68**
	58·19	**5·22**	**5·19**
	60·90	**5·40**	**5·52 ⇒ this is not homogenous.**

CHAPTER ELEVEN

CRYSTAL STRUCTURES

INTRODUCTION

During the synthetic procedures, previously described in this project, a number of interesting complexes were isolated and structurally characterised.

COMPLEX 132

HEXAKIS(N,N-DIMETHYLFORMAMIDE)NICKEL(II)-DIPERCHLORATE

Crystals of hexakis(*N,N*-dimethylformamide)nickel(II)-diperchlorate $[Ni(dmf)_6](ClO_4)_2$ (complex **132**) (Fig. 11·1) were isolated after ether diffusion into a dmf solution of a macrocyclic nickel complex. Identical crystals have since been obtained as by-products of several macrocyclic syntheses.[242] $[Ni(dmf)_6](ClO_4)_2$ is a potential source of anhydrous Ni^{2+} as it can be readily prepared and is surprisingly airstable.

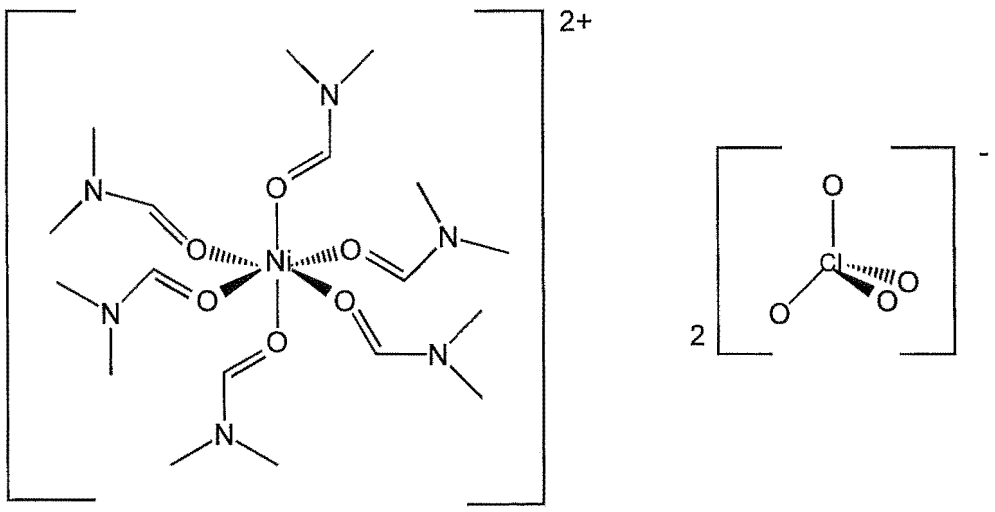


Figure 11·1

The asymmetric unit contains two independent ClO_4^- anions and two independent halves of the $[Ni(dmf)_6]^{2+}$ cation, with each Ni^{2+} ion being located on a centre of symmetry. The two cations differ in the orientation of the the dmf ligands.

In the cation, in which Ni1 is the central ion, each dmf molecule has a different geometry with respect to the others in the cation. The dihedral angles between the a plane through the each dmf ligand and the Ni····O bonds to the remaining ligands all differ. The dihedral angle to a mean plane through the first dmf (*i.e.* the mean plane of O11, C11, N11, C12 and C13) is 9·39°; the angle to the plane of O21, C21, N21, C22 and C23 is 136·46° and to the plane of O31, C31, N31, C32 and C33 is 42·71° (Fig. 11·2).

In contrast, in the cation, centred on Ni2, the planes containing each dmf molecule approximately bisect the (dmf)O····Ni····O(dmf) angle involving the other two independent dmf ligands (*e.g.* the mean plane of O41, C41, N41, C42 and C43 approximately bisects the O51····Ni2····O61 angle; the dihedral angle being 40·77°) (Fig. 11·2).

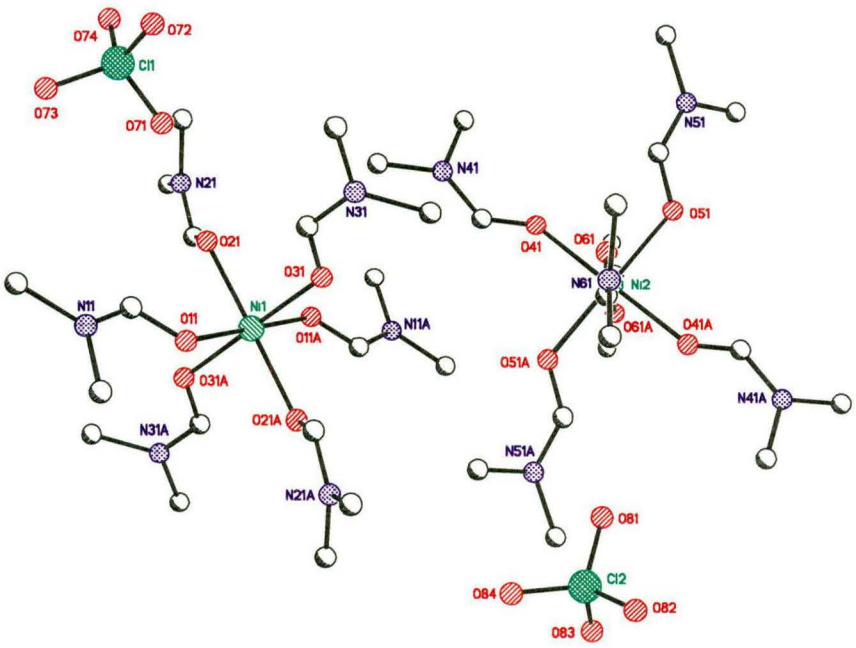


Figure 11·2

The packing diagram (Fig. 11·3) illustrates that no interactions between the cations or between the cations and the perchlorate anions were found.

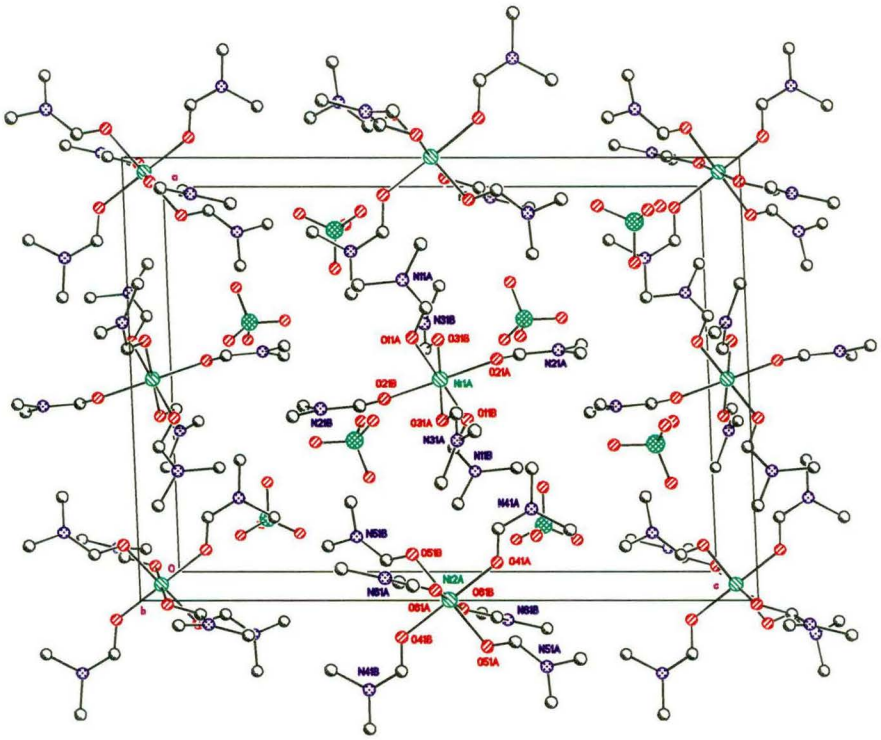


Figure 11·3 : Packing diagram for Complex 132

A search of the April 1995 release of the Cambridge Structural Database [243] showed no previous determinations of the $[Ni(dmf)_6]^{2+}$ ion, although a number of related iron complexes have been reported. $[Fe(dmf)_6](ClO_4)_2$ is isomorphous with the present complex[244]. The iron(III) analogue $[Fe(dmf)_6](ClO_4)_3$ has also been structurally characterised, [245] this cation is centrosymmetric and has the same configuration as that at Ni1, with one pair of dmf ligands "eclipsed" with respect to one of the other Ni····O bonds.

Table 11·1
Selected bond lengths (Å) and bond angles (°) for Complex 132

Ni(1)-O(11)	2·078 (3)	Ni(1)-O(21)	2.057 (3)
Ni(1)-O(31)	2.044 (3)	Ni(1)-O(11A)	2.078 (3)
Ni(1)-O(21A)	2.057 (3)	Ni(1)-O(31A)	2.044 (3)
Ni(2)-O(41)	2.044 (3)	Ni(2)-O(51)	2.053 (3)
Ni(2)-O(61)	2.046 (3)	Ni(2)-O(41A)	2.044 (3)
Ni(2)-O(51A)	2.053 (3)	Ni(2)-O(61A)	2.046 (3)

O(11)-Ni(1)-O(21)	93·5(1)	O(11)-Ni(1)-O(31)	89·7(1)
O(21)-Ni(1)-O(31)	90·8(1)	O(11)-Ni(1)-O(11A)	180·0(1)
O(21)-Ni(1)-O(11A)	86·5(1)	O(31)-Ni(1)-O(11A)	90·3(1)
O(11)-Ni(1)-O(21A)	86·5(1)	O(21)-Ni(1)-O(21A)	180·0(1)
O(31)-Ni(1)-O(21A)	89·2(1)	O(11A)-Ni(1)-O(21A)	93·5(1)
O(11)-Ni(1)-O(31A)	90·3(1)	O(21)-Ni(1)-O(31A)	89·2(1)
O(31)-Ni(1)-O(31A)	180·0(1)	O(11A)-Ni(1)-O(31A)	89·7(1)
O(21A)-Ni(1)-O(31A)	90·8(1)	O(41)-Ni(2)-O(51)	87·9(1)
O(41)-Ni(2)-O(61)	90·7(1)	O(51)-Ni(2)-O(61)	90·7(1)
O(41)-Ni(2)-O(41A)	180·0(1)	O(51)-Ni(2)-O(41A)	92·1(1)
O(61)-Ni(2)-O(41A)	89·3(1)	O(41)-Ni(2)-O(51A)	92·1(1)
O(51)-Ni(2)-O(51A)	180·0(1)	O(61)-Ni(2)-O(51A)	89·3(1)
O(41A)-Ni(2)-O(51A)	87·9(1)	O(41)-Ni(2)-O(61A)	89·3(1)
O(51)-Ni(2)-O(61A)	89·3(1)	O(61)-Ni(2)-O(61A)	180·0(1)
O(41A)-Ni(2)-O(61A)	90·7(1)	O(51A)-Ni(2)-O(61A)	90·(1)

EXPERIMENTAL

Ether was diffused into dmf solutions of macrocyclic nickel complexes. Nickel, which had not been incorporated into the complexes was isolated as $[Ni(dmf)_6]\cdot(ClO_4)_2$. Identical crystals were obtained as serendipitous products from several different macrocyclic syntheses .

Table 11·2 : Crystal data and structure refinement for Complex 132

Empirical formula	C18 H42 Cl2 N6 Ni O14	
Formula weight	696.19	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 14.843(6) Å	alpha = 90°.
	b = 10.797(4) Å	beta = 92.26(4)°
	= 20.728(10) Å	gamma = 90°
Volume, Z	3319(2) $Å^3$, 4	
Density (calculated)	1.393 Mg/m^3	
Absorption coefficient	0.811 mm^{-1}	
F(000)	1464	
Crystal colour and form	blue-green block	
Crystal size	0.7 x 0.6 x 0.4 mm	
Theta range for data collection	2.13 to 25.00 deg.	
Limiting indices	0<h<17, 0<k<12, -24<l<24	
Reflections collected	6076	
Independent reflections	5849 [R(int) = 0.0191]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5849 / 0 / 373	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0516, wR2 = 0.1220	
R indices (all data)	R1 = 0.0785, wR2 = 0.1323	
Largest diff. peak and hole	0.569 and -0.457 e.A^-3	

COMPLEX 133 : POTASSIUM PHTHALATE

Crystals of potassium phthalate were isolated from the synthesis of 1,8-diamino-octan-3,6-diol after the phthalimide step (Chapter 9). In this step the chloride ions in 1,8-dichloro-octan-3,6-dione are replaced with phthalimide. Subsequent treatment results in the formation of the diamine. It is apparent that some of the potassium phthalimide has opened to form the potassium salt of phthalic acid (Fig. 11·4). One molecule is found in the asymmetric unit.

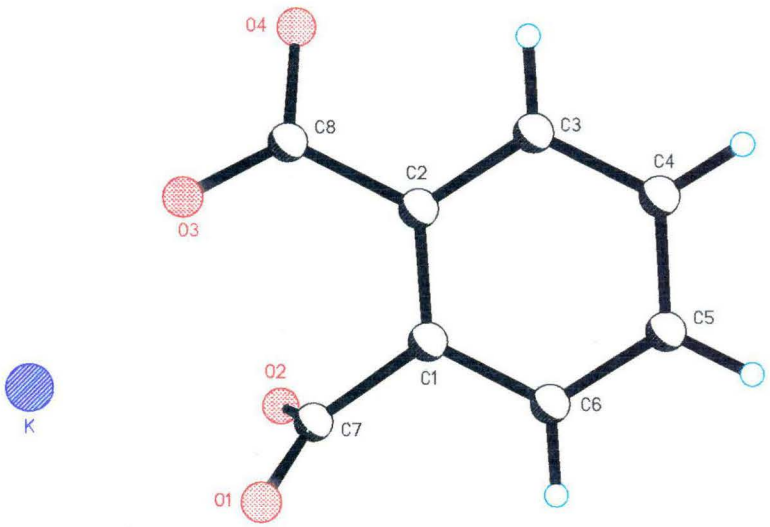


Figure 11·4

Atoms C1 through to C8 (0·0013 Å mean deviation from the plane) with the carboxylate groups twisted 29·7° and 106·1°out of this plane.

Distances between oxygen (with the exception of O4) and potassium atoms are consistent with strong electrostatic interactions (2·63 to 3·11 Å). The packing diagram of complex **133** (Fig. 11·5) reveals that the phthallic acid anions are arranged in columns through the crystal with the potassium ions found between the columns.

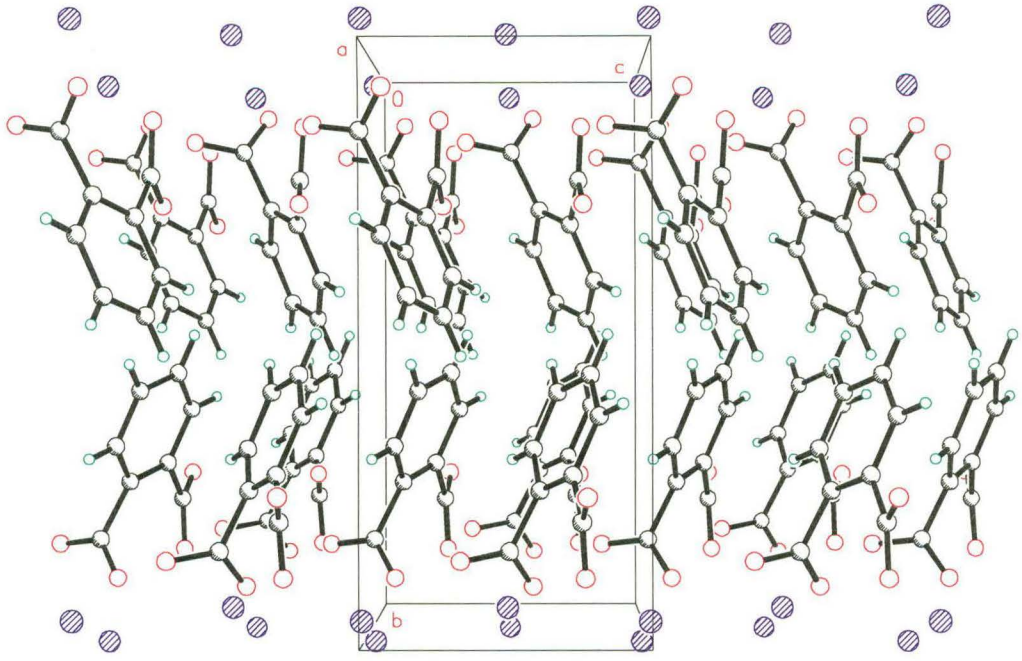


Figure 11·5 : Crystal Packing of Complex 133

A considerable number of phthalic acid structures were found in the Cambridge Data base and a number of these were of the potassium, sodium or lithium salts.

Table 11·2
Selected bond lengths [A] and angles [°] for Complex 133

K-O(2)	2.772(2)	K-O(3)	2.842(2)	K-O(1)	2.970(3)
K-C(7)	3.044(3)	O(3)-C(8)	1.226(4)	O(4)-C(8)	1.301(5)
C(7)-O(1)	1.230(4)	C(7)-O(2)	1.274(5)	C(7)-O(2)	1.274(5
K-O(2)	2.772(2)	K-O(3)	2.842(2)	K-O(1)	2.970(3)
K-C(7)	3.044(3)	O(3)-C(8)	1.226(4)	O(4)-C(8)	1.301(5)
C(7)-O(1)	1.230(4)				

O(2)-K-O(3)	67.45(7)	O(2)-K-O(1)	45.36(6)
O(3)-K-O(1)	65.86(8)	O(2)-K-C(7)	24.74(9)
O(3)-K-C(7)	56.03(8)	O(1)-K-C(7)	23.56(8)
C(8)-O(3)-K	138.7(2)	O(1)-C(7)-O(2)	125.1(3)
O(1)-C(7)-C(1)	117.9(3)	O(2)-C(7)-C(1)	117.1(3)
O(1)-C(7)-K	74.9(2)	O(2)-C(7)-K	65.6(2)
C(7)-O(1)-K	81.6(2)	O(3)-C(8)-O(4)	124.5(4)
O(3)-C(8)-C(2)	121.1(4)	O(4)-C(8)-C(2)	114.3(2)

Symmetry transformations used to generate equivalent atoms:
#1 x-1/2,-y+2,z #2 -x+2,-y+2,z-1/2 #3 -x+2,-y+2,z+1/2
#4 -x+3/2,y,z-1/2 #5 x+1/2,-y+2,z

EXPERIMENTAL

Potassium phthalimide was vigourously stirred in dry dmf and 1,8-dichloro-octan-3,6-dione dissolved in a little dmf was added dropwise to the reaction mixture. The mixture was heated to 80° C in an oil bath and left stirring for 14 h and left to sit 5 h. A brown solid was filtered from the mixture, stirred in $CHCl_3$, and refiltered. The pale yellow filtrate was set aside and crystals of potassium phthalate were separated from this.

Table 11·4 :Crystal data and structure refinement for 133

Empirical formula	C7H10K2O4	
Formula weight	236·35	
Temperature	158(2) K	
Wavelength	0.71073 A	
Crystal system	Orthorhombic	
Space group	Pca2(1)	
Unit cell dimensions	a = 9.575(3) A	alpha = 90 deg.
	b = 13.220(4) A	beta = 90 deg.
	c = 6.416(2) A	gamma = 90 deg.
Volume, Z	812·2(4) $Å^{3,}$ 4	
Density (calculated)	1·933 Mg $m^{3\,-1}$	
Absorption coefficient	1·141 mm^{-1}	
F(000)	488	
Crystal size	0·7 x 0·52 x 0·28 mm	
Crystal form and colour	Pale yellow block	
Theta range for data collection	2.63 to 25.01 deg.	
Limiting indices	-11<h<11, -15<k<1, -7<l<7	
Reflections collected	3024	
Independent reflections	1432 [R(int) = 0.1115]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1432 / 1 / 118	
Goodness-of-fit on F^2	0.936	
Final R indices	[I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0861
R indices (all data)	R1 = 0.0370, wR2 = 0.0870	
Absolute structure parameter-	0.07(6)	
Largest diff. peak and hole	0.391 and -0.279 e.A^-3	

COMPLEX 134 : 2,6-DIFORMYL-4-METHYLPHENOL

Crystals of 2,6-diformyl-4-methylphenol (dfmp) (compound **134**) (Fig. 11·6) were isolated as fine pale yellow needles from a reaction mixture in which dfmp, dahp and HCl had been refluxed together in an attempt to form the protonated ligand H_4LV5. One molecule is found in the asymmetric unit. A plane is found through the molecule (mean deviation from the plane is 0·006 Å).

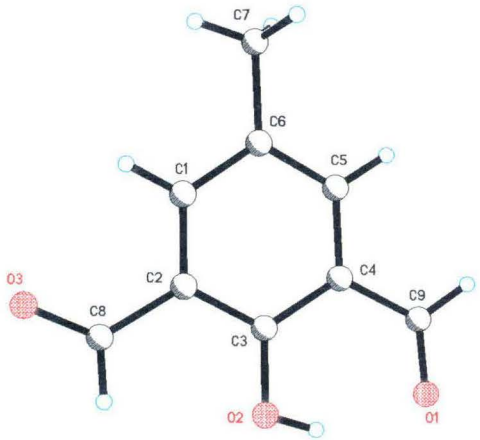


Figure 11·6

Π-stacking occurs between adjacent molecules (Fig. 11·7) in the crystal structure with the carbon - carbon distances between the molecules ranging from 3·369 to 3·483 Å.

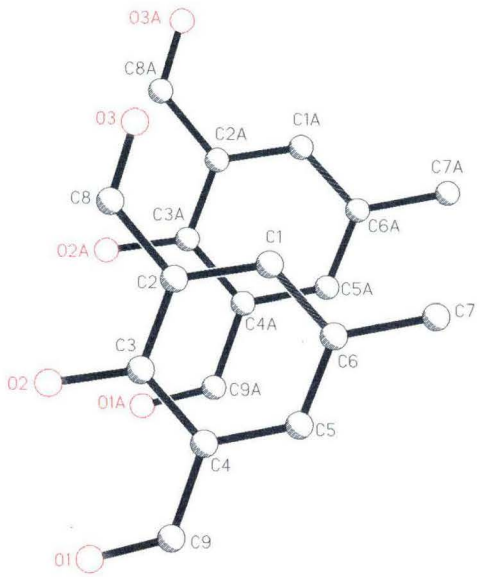


Figure 11·7

The packing diagrams (Figs. 11·8 & 11·9) reveal that the molecules are arranged in pairs of columns extending throughout the crystal and with intercolumnar hydrogen bonding.

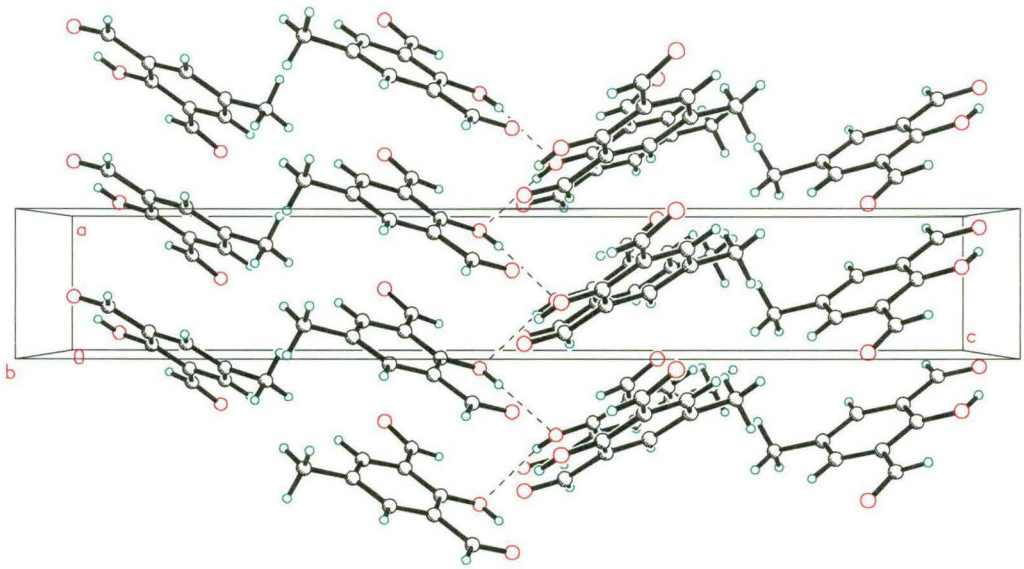


Figure 11·8 : Packing diagram for Complex 11·3

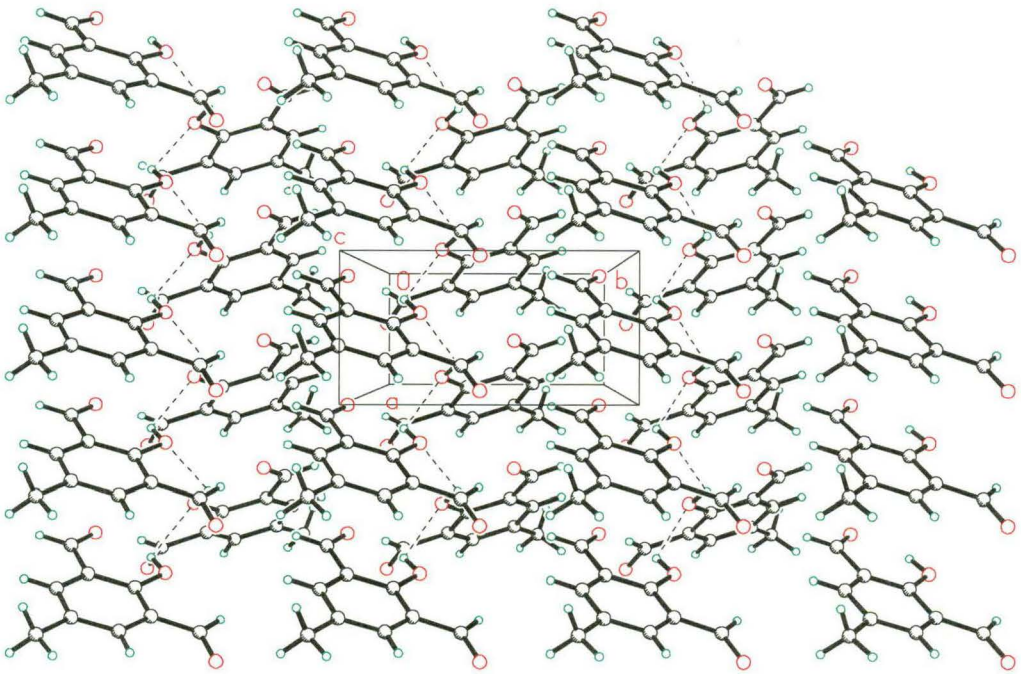


Figure 11·9 : Packing diagram for Complex 134

A Cambridge Data base search revealed that the crystal structure of dfmp has been reported in three isomeric forms one of which is clearly the same as the polymorph complex **134** [246]. The only other structure in which the dfmp fragment was seen was in the following crown ether complex (Fig. 11·10).[247]

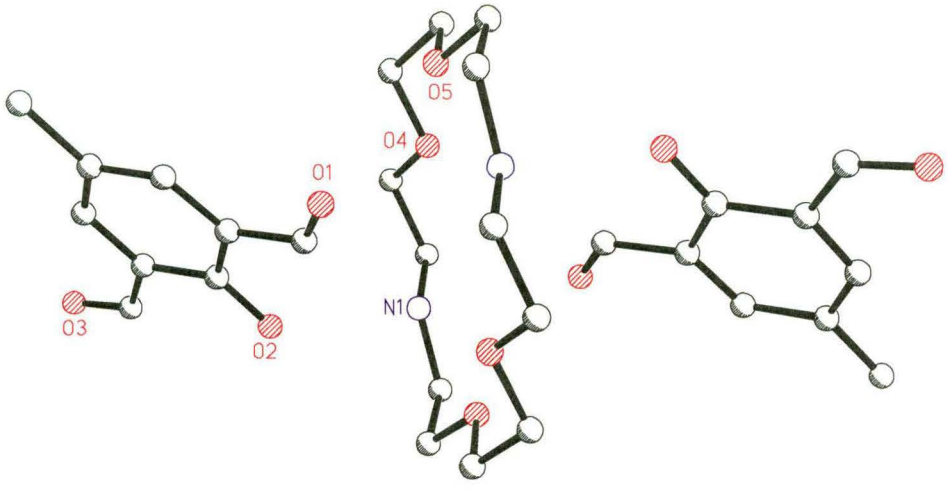


Figure 11·10

Table 11·5 :
Selected bond lengths [A] and angles [°] for Complex 134

C(3)-O(2	1.345(4)	C(8)-O(3	1.219(4)	C(9)-O(1	1.230(4)

C(6)-C(1)-C(2	123.1(3)	C(1)-C(2)-C(3	119.0(3)
O(2)-C(3)-C(2	118.4(3)	O(2)-C(3)-C(4	122.4(3)

EXPERIMENTAL

Extremely pale yellow fine needle-like crystals were formed after the reduction, under vacuum, of a reaction mixture in which dfmp (2 mmol), dahp (2 mmol) and HCl (8 mmol) had been refluxed together for 24 h. X-ray structure analysis showed them to be the dfmp starting material.

Table 11·6 :Crystal data and structure refinement for 134

Empirical formula	C10H8O3
Formula weight	176.16
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 3.8900(10) Å alpha = 90 deg.
	b = 7.540(2) Å beta = 90 deg.
	c = 25.978(5) Å gamma = 90 deg.
Volume, Z	762.0(3) $Å^3$, 4
Density (calculated)	1.536 Mg/m^3
Absorption coefficient	0.114 mm^{-1}
F(000)	368
Crystal colour and form	Pale yellow block
Crystal size	0.82 x 0.24 x 0.14 mm
Theta range for data collection	2.81 to 25.00 deg.
Limiting indices	0<h<4, -2<k<8, -2<l<30
Reflections collected	1121
Independent reflections	1057 [R(int) = 0.0095]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1057 / 0 / 109
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1165
R indices (all data)	R1 = 0.0685, wR2 = 0.1293
Absolute structure parameter	-5(3)
Largest diff. peak and hole	0.281 and -0.315 $e.Å^{-3}$

COMPLEX 135 : 1,5-DIAMINOPENTAN-3-ONE DIHYDROCHLORIDE

The synthesis of 1,5-diaminopentan-3-ol dihydrochloride (dahp) was undertaken (Chapter 2). In the third step of this synthesis 1,5-diphthalimidopentan-3-one is conveted to 1,5-diaminopentan-3-one dihydrochloride. During the isolation of the ketone, crystals were formed and X-ray structure analysis was undertaken. Two independent molecules are found in the asymmetric unit (Fig.11·11).

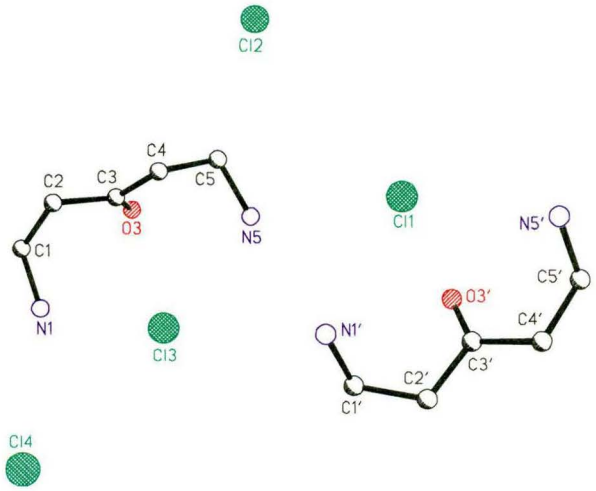


Figure 11·11 : Complex 135

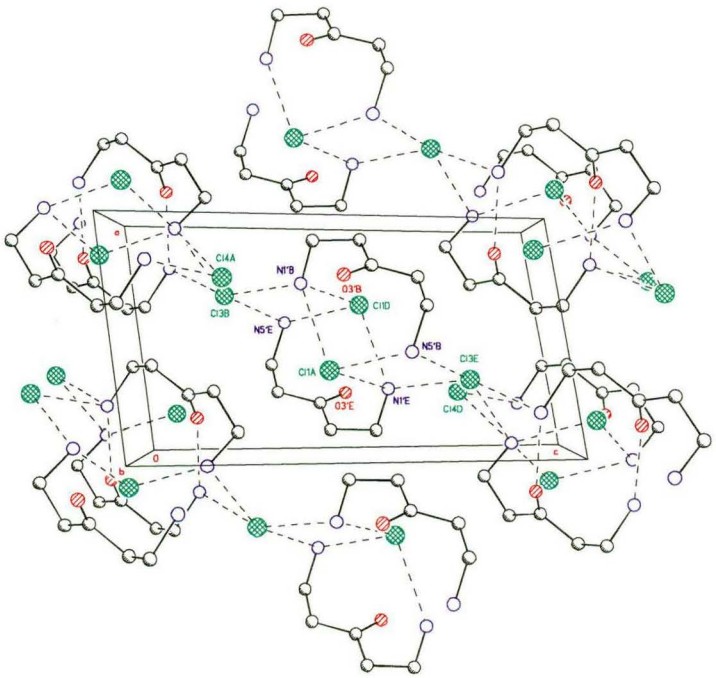


Figure 11·12 : Packing diagram for Complex 135

Details of the packing of this crystal (Fig. 11·12) shows the extensive potential hydrogen bonding interactions between the nitrogen atoms and the chloride ions. Each nitrogen atom interacts with three chloride ions with the distances ranging from 3·130 Å to 3·278 Å.

A Cambridge Data Base search showed that this structure has not been previously reported

Table 11·7 :
Selected bond lengths [A] and angles [°] for Complex 135

O(3)-C(3)	1·211(12)	N(1)-C(1)	1·462(13)	N(5)-C(5)	1·490(13)
C(1)-C(2)	1·516(14)	C(2)-C(3)	1·505(14)	C(3)-C(4)	1·517(13)
C(4)-C(5)	1·508(14)				

N(1)-C(1)-C(2)	111·0(8)	C(3)-C(2)-C(1)	112·7(9)
O(3)-C(3)-C(2)	122·4(9)	O(3)-C(3)-C(4)	121·2(9)
C(2)-C(3)-C(4)	116·3(8)	C(5)-C(4)-C(3)	113·5(8)
N(5)-C(5)-C(4)	111·8(8)		

EXPERIMENTAL

1,5-Diaphthalimidopentan-3-one (189·87 g, 0·509 mol) was boiled in a mixture of acetic acid (475 mL) and conc. HCl (306 mL) with additional 17 mL aliquots of conc. HCl being added at 8 hourly intervals over a period of 3 days until 170 mL had been added. On cooling, the fawn precipitate of phthalic acid was filtered off and washed with water. The combined filtrates and washings were evaporated nearly to dryness under reduced pressure, ~ 400 mL of water added and the undissolved phthalic acid filtered off. The filtrate was concentrated to ~50 mL under vacuum, ~700 mL of ethanol added and the resulting white precipitate, 1,5-diaminopentan-3-one dihydrochloride collected in a frit under vacuum. The ketone was washed with EtOH to remove any remaining phthalic acid. Crystals separated from the ketone were suitable for X-ray structure analysis.

Table 11·8 :Crystal data and structure refinement for 135

Empirical formula	C5H12Cl2N2O	
Formula weight	187·07	
Temperature	158(2) K	
Wavelength	0·71073 Å	
Crystal system	monoclinic	
Space group	P-1	
Unit cell dimensions	a = 7·795(5) Å	α= 106·36(4) deg.
	b = 8·850(5) Å	β = 94·47(5) deg.
	c = 14·330(9) Å	γ = 103·76(4) deg.
Volume, Z	910·1(10) $Å^3$, 4	
Density (calculated)	1·365 Mg m^{-3}	
Absorption coefficient	0·656 mm^-1	
F(000)	392	
Theta range for data collection	2·48 to 22·50 deg.	
Limiting indices	-8<h<0, -8<k<8, -15<l<15	
Reflections collected	2415	
Independent reflections	2333 [R(int) = 0·3361]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2333 / 0 / 160	
Goodness-of-fit on F^2	1·295	
Final R indices [I>2sigma(I)]	R1 = 0·1229, wR2 = 0·3158	
R indices (all data)	R1 = 0·1441, wR2 = 0·3332	
Largest diff. peak and hole	2·392 and -2·688 e.Å^-3	

COMPLEX 136 :

TETRAKIS-(TRIMETHYLAMMONIUM)HEXATHIOCYANATONICKEL(II)

Crystals of Tetrakis-(trimethylammonium)hexakis-(isothiocyanato)-nickel(II) $[Ni(NCS)_6]^{4-}\cdot[(CH_3)_3NH]^+_4$ (Fig. 11·14) were isolated from the treated filtrate of a macrocyclic nickel complex.

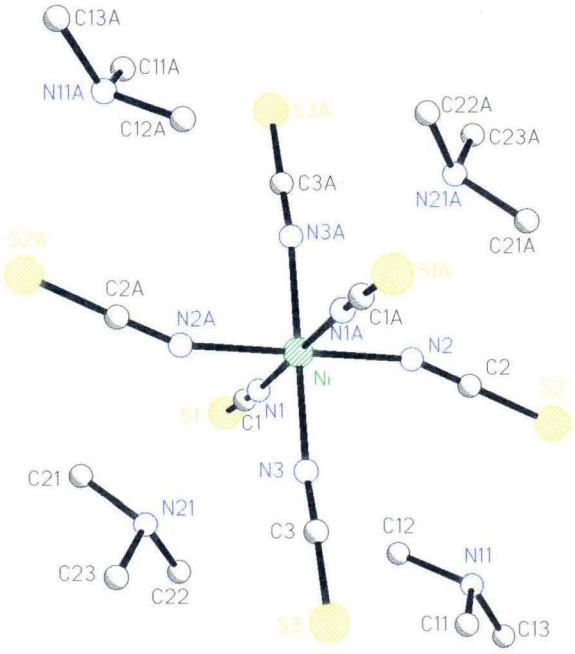


Figure 11·12 : Complex 136

The asymmetric unit contains half of a $[Ni(NCS)_6]^{4-}$ anion and two independent $[(CH_3)_3N]^+$ cations. The Ni^{2+} cation is located on a centre of symmetry. In the hexathiocyanatonickel(II) cation the coordination geometry around the nickel ion is close to octahedral with the angles ranging from 89·2 to 90·8° (Fig. 11·13). The S1 - C1 - N1 are nearly linear.

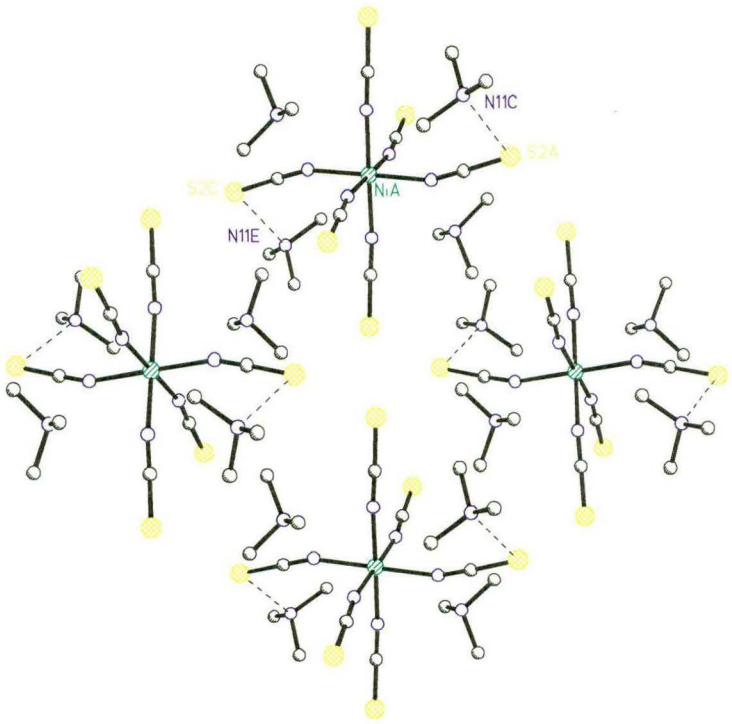


Figure 11·13 : Packing diagram for Complex 136

Two of the trimethyl ammonium ions are 3·247 Å from sulfur atoms to which they could be considered to be weakly hydrogen bonded.

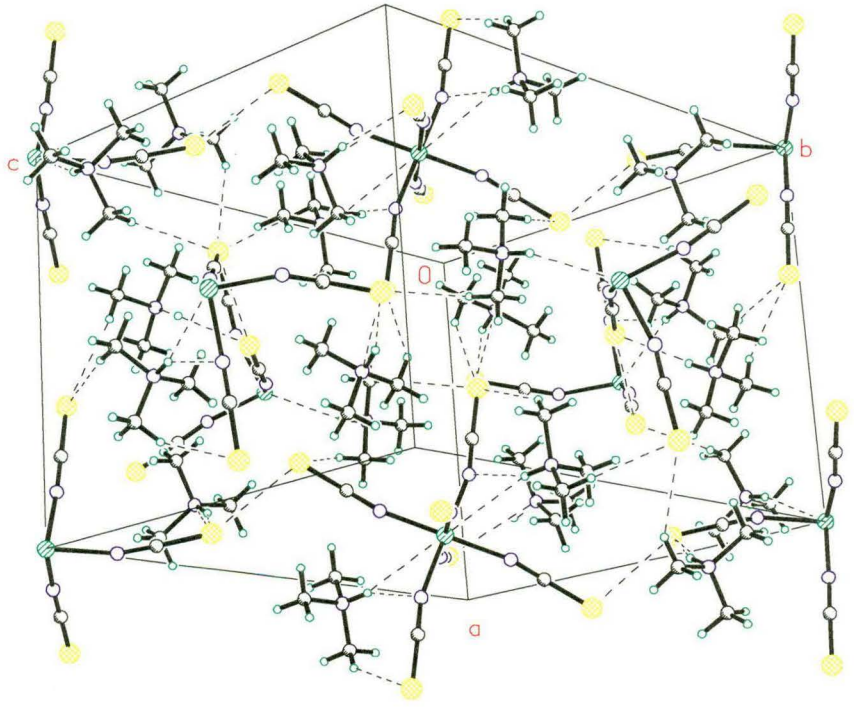


Figure 11·14 : Packing diagram for Complex 136

A Cambridge Data base search showed that two crystal structures involving the hexakis(isothiocyanato)-nickel(II) cation and an ammonium ion have been reported. In 1982 the structure of of tetrakis-(tetramethylammonium) hexakis-(isothiocyanato)-nickel(II) was deposited[248]. More recently the structure is tetrakis- (triethylammonium) hexakis(isothiocyanato)-nickel(II) has been reported[249].

Table 11·9
Selected bond lengths [A] and angles [°] for Complex 136

Ni-N(2)	2·055(2)	Ni-N(1)	2·071(2)	Ni-N(3)	2·077(2)
N(11)-C(13)	1·486(3)	N(1)-C(1)	1·154(3)	N(2)-C(2)	1·148(3)
N(3)-C(3)	1·150(3)	C(2)-S(2)	1·639(3)	C(3)-S(3)	1·626(2)
N(21)-C(22)	1·464(4)	N(21)-C(21)	1·469(3)	N(21)-C(23)	1·478(3)
C(1)-S(1)	1·630(3)	N(11)-C(12)	1·478(3)	N(11)-C(11)	1·478(3)

N(2)-Ni-N(1)	89·25(9)	N(2)-Ni-N(3)	90·26(9)
N(1)-Ni-N(3)	90·17(8)	C(1)-N(1)-Ni	168·5(2)
C(2)-N(2)-Ni	159·5(2)	C(3)-N(3)-Ni	164·7(2)
N(2)-C(2)-S(2)	177·9(2)	N(3)-C(3)-S(3)	178·3(2)
C(22)-N(21)-C(21)	111·6(2)	C(22)-N(21)-C(23)	110·0(3)
C(21)-N(21)-C(23)	110·5(2)	N(1)-C(1)-S(1)	178·7(2)
C(12)-N(11)-C(11)	111·6(2)	C(12)-N(11)-C(13)	111·8(2)
C(11)-N(11)-C(13)	111·2(2)		

EXPERIMENTAL

The filtrate of a nickel(II) macrocyclic reaction mixture, which had been treated with NH_4NCS, had dried to a green oily mass coated with a "plastic" crust. On addition of a ~5 mL of dry EtOH a green-yellow solid and blue-green crystals were isolated by filtration and separated by hand. An IR spectrum of the crystals showed them not to be $Ni(NO_3)_2$ (one of the starting materials for the macrocyclic reaction) and X-ray structure analysis was undertaken.

Table 11·10 :Crystal data and structure refinement for 136

Empirical formula	C9H20N5Ni0.50S3	
Formula weight	323·83	
Temperature	293(2) K	
Wavelength	0·71073 A	
Crystal system	orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 12·078(2) Å	α = 90 deg.
	b = 14·609(3) Å	β = 90 deg.
	c = 18·149(4) Å	γ = 90 deg.
Volume, Z	3202·3(11) $Å^3$, 8	
Density (calculated)	1·343 Mg m^{-3}	
Absorption coefficient	1·023 mm^{-1}	
F(000)	1368	
Crystal colour and form	blue-green chunk	
Crystal size	0·64 x 0·60 x 0·56? mm	
Theta range for data collection	2.24 to 25.00 deg.	
Limiting indices	-14<h<1, -1<k<17, -1<l<21	
Reflections collected	3284	
Independent reflections	2818 [R(int) = 0.0138]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2818 / 0 / 162	
Goodness-of-fit on F^2	1·061	
Final R indices [I>2sigma(I)]	R1 = 0·0323, wR2 = 0·0724	
R indices (all data)	R1 = 0·0444, wR2 = 0·0782	
Largest diff. peak and hole	0·551 and -0·479 e.$Å^3$	

Complex 137

BISACETONITRILOTETRAAQUACOBALT(II) TETRACHLOROCOBALTATE

Bisacetonitrilotetraaquacobalt(II) tetrachlorocobaltate was isolated from a solution formed when the frits and flasks, from which a final reaction product had been filtered, were rinsed with CH_3CN and the blue-green solution set up for ether diffusion. The crystals were bright green. The asymmetric unit contains one $CoCl_4^{2-}$ anion and one $[Co(CH_3CN)_2(H_2O)_4]^{2+}$ cation (Fig. 11·15). Coordination geometry in the $[Co(CH_3CN)_2(H_2O)_4]^{2+}$ cation is octahedral with the angles around the cobalt ion ranging from 88·5 to 92·1 °. The acetonitrile molecules are coordinated in the axial positions and the water molecules are arranged in the equatorial plane. The $CoCl_4^{2-}$ anion is a tetrahedral moeity.

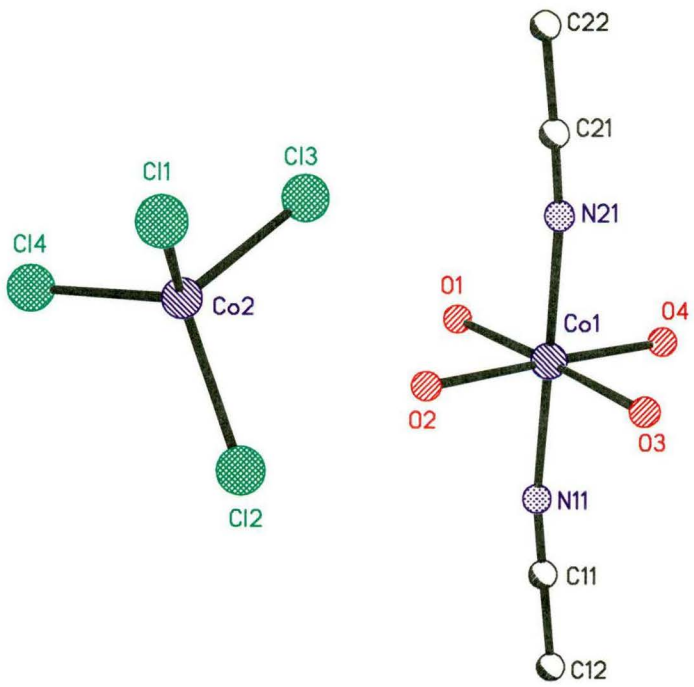


Figure 11·15 : Complex 137

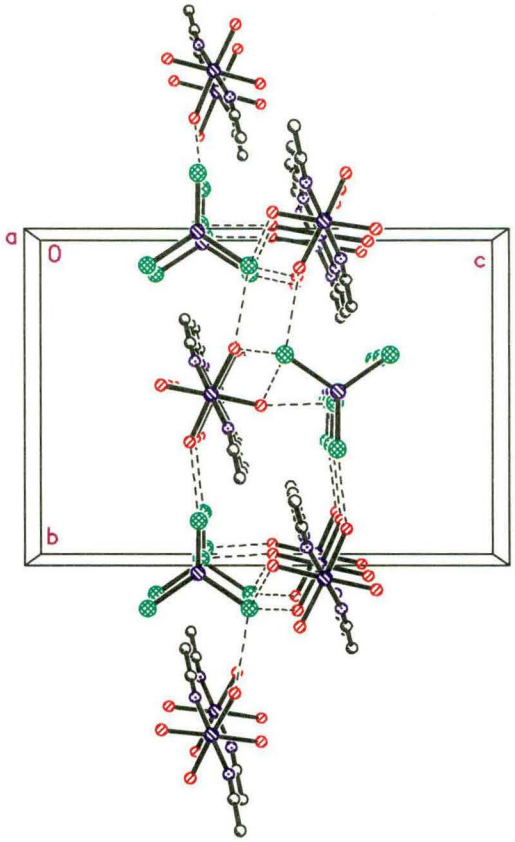


Figure 11·15 : Packing diagram for Complex 137

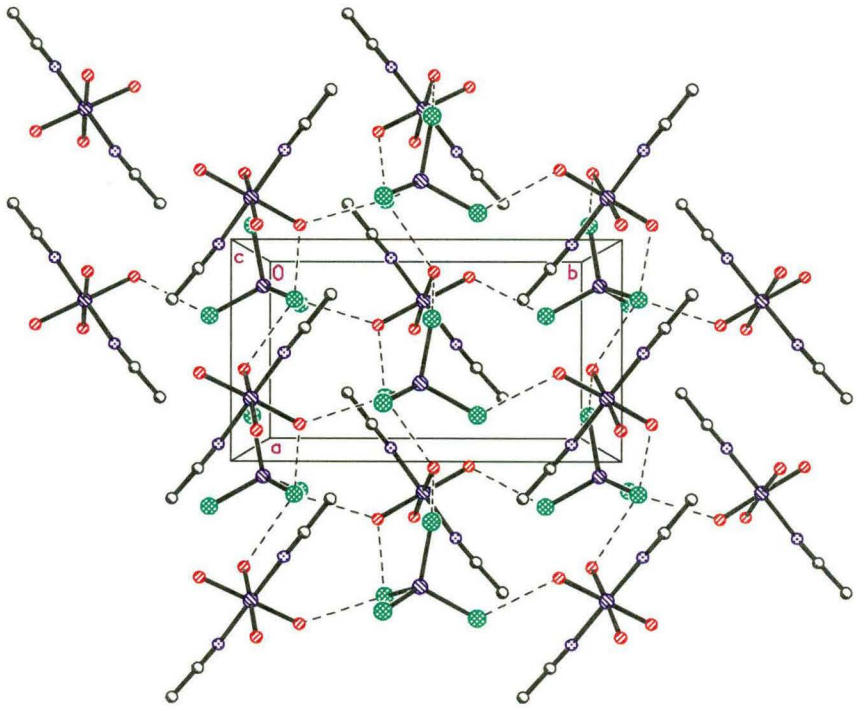


Figure 11·16 : Packing diagram for Complex 137

Figures 11·15 and 11·16 show the crystal packing and potential hydrogen bonding interactions. The molecules within the crystal such that cations and anions alternate within rows parallel with the unit cell edges.

Figure 11·17 shows details of the possible hydrogen bonding interactions. Two oxygen atoms in each cation form hydrogen bonds with two of the chloride ions of the anions.

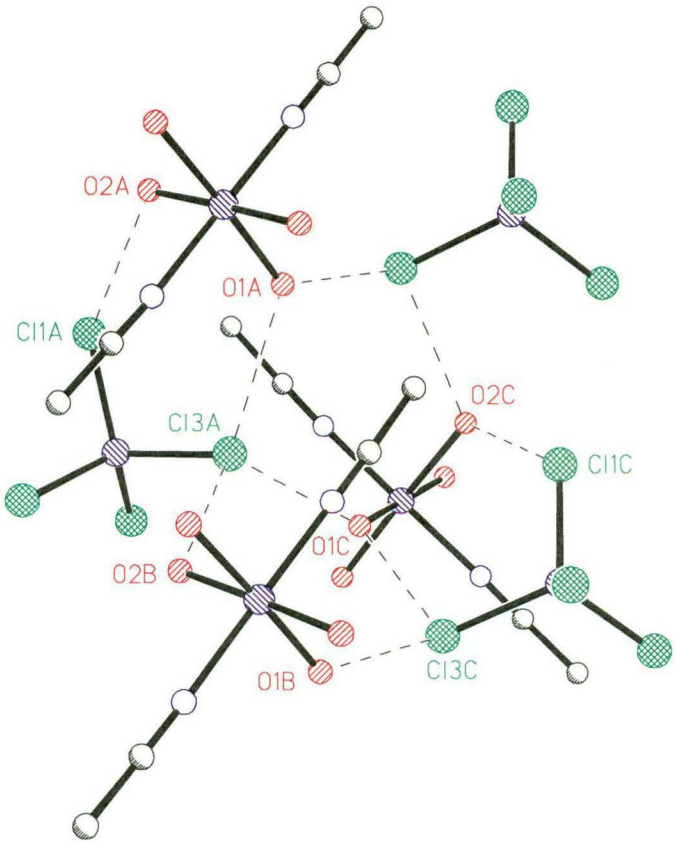


Figure 11·17

No structure containing this cation has been deposited with the Cambridge data base.

Table 11·11
Selected bond lengths [A] and angles [°] for Complex 137

Co(1)-O(1)	2·09(5)	Co(1)-O(3)	2·05(5)	Co(2)-Cl(3)	2·301(13)
Co(1)-O(4)	2·07(4)	Co(1)-N(21)	2·19(4)	Co(2)-Cl(4)	2·223(14)
Co(1)-O(2)	2·13(4)	Co(1)-N(11)	1·98(5)	Co(2)-Cl(1)	2·279(13)
Co(2)-Cl(2)	2·266(12)				

O(1)-Co(1)-O(3)	176(3)	O(1)-Co(1)-O(4)	90(2)
O(3)-Co(1)-O(4)	94(2)	O(1)-Co(1)-N(21)	93(3)
O(3)-Co(1)-N(21)	87(3)	O(4)-Co(1)-N(21)	95(2)
O(1)-Co(1)-O(2)	87(2)	O(3)-Co(1)-O(2)	89(2)
O(4)-Co(1)-O(2)	176(2)	N(21)-Co(1)-O(2)	82(2)
O(1)-Co(1)-N(11)	89(3)	O(3)-Co(1)-N(11)	92(2)
O(4)-Co(1)-N(11)	91(2)	N(21)-Co(1)-N(11)	173(2)
O(2)-Co(1)-N(11)	92(2)		

EXPERIMENTAL

A synthesis for a macrocyclic complex of LV5 and $CoCl_2$ was set up in the usual manner and the product filtered from the reaction mixture. The filtrate was set aside and eventually a second product was isolated. The reaction vessel and frit were rinsed with acetonitrile and the resulting blue-green solution set up for ether diffusion. Bright green crystals were isolated from this solution.

Table 11·12 :Crystal data and structure refinement for 137

Empirical formula	C8H28Cl8Co4N4O8
Formula weight	827.66
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 7.0250(10) Å alpha = 90 deg.
	b = 12.3090(10) Å beta = 90 deg.
	c = 17.924(2) Å gamma = 90 deg.
Volume, Z	1549.9(3) $Å^3$, 2
Density (calculated)	1.773 Mg/m^3
Absorption coefficient	2.828 mm^{-1}
F(000)	824
Crystal colur and form	Bright green block
Crystal size	0.78 x 0.29 x 0.19 mm
Theta range for data collection	2.01 to 27.51 deg.
Limiting indices	-1<h<9, -1<k<15, -23<l<23
Reflections collected	4695
Independent reflections	3558 [R(int) = 0.0422]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3557 / 0 / 145
Goodness-of-fit on F^2	6.854
Final R indices [I>2sigma(I)]	R1 = 0.3897, wR2 = 0.7341
R indices (all data)	R1 = 0.4164, wR2 = 0.7551
Absolute structure parameter	0.6(3)
Largest diff. peak and hole	33.169 and -9.066 $e.Å^{-3}$

COMPLEX 138

A number of syntheses involving the LV5 ligand system and iron salts were tried (Chapter 9). Golden brown crystals formed in the filtrate of one of the Fe(III) preparations and X-ray crystal structure analysis of them was carried out. It was revealed that the dialdehyde groups of the phenol starting material had been oxidised by the iron to the corresponding carboxylates (Fig. 11·18)

Four independent molecules are found in the asymmetric unit of this structure. At the time of writing the refinement is converged at R = 0.086. The carboxylate carbons all exhibit disorder which is yet to be modelled. The equivalence of the carbon - oxygen bonds in the carboxylate groups means that the hydrogen atoms for each of these groups will be averaged across two positions and they also have not yet been included in the refinement.

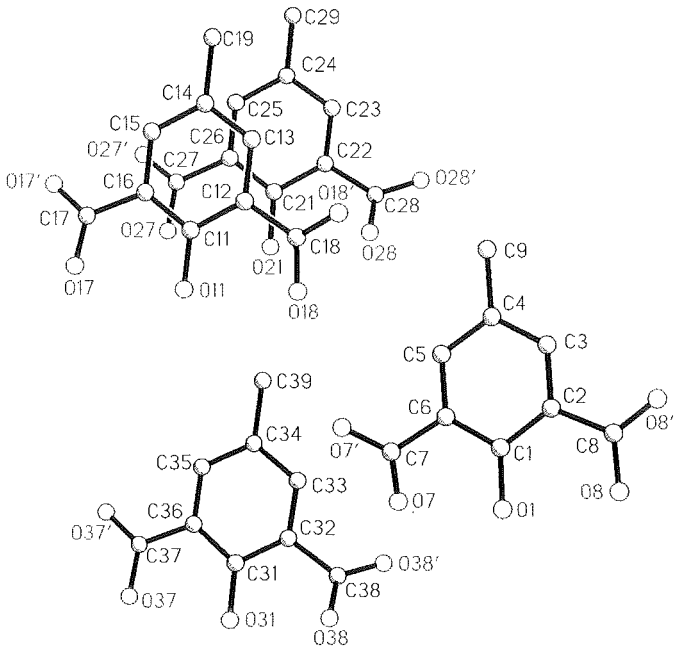


Figure 11·18 :

EXPERIMENTAL

A synthesis was set up using dfmp, dahp and $Fe(III)(ClO_4)_3$ as the templating salt. The mixture was refluxed for 24 h after which time a rust brown microcrystalline material was filtered from the reaction mixture. This material has not been identified. The brown filtrate was set aside and within two days golden brown crystals formed in this solution.

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

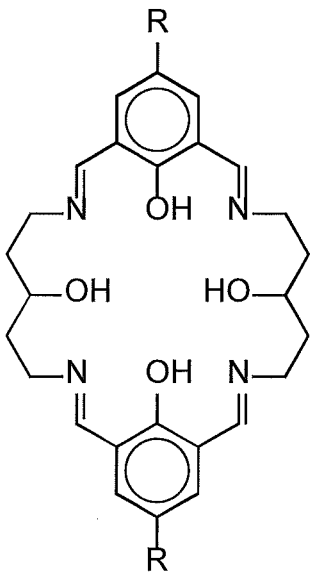


Figure 1 : H_4**LV5** : R = CH_3, H_4**LV5t** : R = $C(CH_3)_3$

Schiff-base template condensation of 2,6-diformyl-4-methylphenol (dfmp) or 2,6-diformyl-4-t-butylphenol (dftp) with 1,5-diaminopentanol (dahp) and a range of transition metal salts to form complexes of **LV5** and **LV5t** were investigated. The starting materials were synthesised and in the course of this project the yield of dahp was improved from 16 % (Lit)[207] to 68 %.

The formation of tetranuclear complexes of this ligand system was a primary aim of this project and the seventy-nine tetranuclear complexes for which formulae have been assigned, are shown in Table 1. They are categorised by the metal salt used in the synthesis (e.g. four cobalt complexes of **LV5** or **LV5t** in which the salt used was the acetate anion, have been assigned formulae). Most have been assigned formulae by the interpretation of spectral (IR and FAB-ms) and micro-analysis. Two copper, one cobalt and one nickel (only partially solved) tetranuclear complexes have been characterised by X-ray crystal structure analysis.

Two octanuclear copper complexes were synthesised and the complex $[\{Cu_4(\mu_5\text{-}O)\mathbf{LV5}(ClO_4)\}_2]\cdot(ClO_4)_2\cdot 4H_2O$, was characterised by X-ray crystal structure analysis.

Table 1

COPPER											
	Perchlorate			Tetrafluorborate							
	B	T	O	B	T						
LV5	1	7	2	0	2						
	Perchlorate			Acetate		Nitrate		Chloride		Thiocyanate	
	B	T		B	T	B	T	B	T	B	T
COBALT											
LV5	7	1		-	4	1	1	8	2	4	2
LV5t	0	0		-	0	0	3	0	3	2	0
Lo-s	3	0		-	0	0	0	1	0		0
				OAc - NCS/N_3							
LV5					4						
LV5t					3						
MANGANESE											
LV5	6	0		0	5	1	1	0	2	-	-
LV5t	1	0		0	1	0	1	0	2	-	-
Lo-s	0	0		2	0	0	0	0	0	-	-
NICKEL											
LV5	1	4		3	2	0	0	0	2	-	-
LV5t	0	3			2	0	0	0	3	-	-
				OAc - NCS/N_3							
LV5t				3	2						
ZINC											
LV5	6	2		-	-	1(tri?)	1	0	2	OAc - NCS/N_3	
LV5t	0	4		-	-	0	4	0	1	2	-
LEAD											
LV5	1	1		-	-	-	-	-	-	-	-
BARIUM											
LV5	2	-		-	-	-	-	-	-	-	-
IRON											
LV5	2	2		-	-	-	-	-	-	-	-

(-) indicates not tried.

Preliminary investigations of the reaction between the tetranuclear copper complexes and catechol indicate that they have catalytic action .

Mixed valence cobalt and manganese systems were synthesised. Table 2 shows a summary of the complexes already prepared when this project began. The asterisks represent the compounds needed to complete the mixed-valence series. All of these except $Mn^{II}_3Mn^{III}$ are believed to have been achieved.

Table 2

Co^{II}_4	*	*	$Co^{II}Co^{III}_3$	*
*	*	$Mn^{II}_2Mn^{III}_2$	*	*

No specific factor influencing the formation of tetranuclear complexes can be clearly identified from these results. The recovery of tetranuclear complexes seems to be enhanced when the anion used is acetate or chloride,* the ligand is **LV5t** and syntheses to which TEA has been added.

New diagonally bridged binuclear cobalt complexes were synthesised. Five binuclear cobalt complexes were characterised by X-ray structure analysis and all show a diagonally chloro-bridged Co(II) core. A total of fifty-seven binuclear complexes (Table 1) have been assigned formulae.

These complexes offer exciting new routes into hetero-tetranuclear complexes . Preliminary investigations of the oxidation cobalt ions in the binuclear Co(II) complexes and tthe insertion of other metals into the vacantt coordination sites have been undertaken.

Identification of the binuclear complexes was aided by the identification of a fingerprint region in the infrared spectra of these products.

It is seems that, at least in solution, there is an equilibrium between the formation of tetranuclear and binuclear species. Which product is recovered appears to be related to a number of factors. Their differing solubilities may be the key to separating them.

Verification, by X-ray crystallographic techniques, of the formulations assigned to the products of these syntheses is the most important thing to be accomplished next in this project. To achieve this it is going to be necessary to further purify them. Some success was achieved by redissolving the products in CH_2Cl_2, filtering and redrying them. Purification is most likely to be achieved by employing column chromatographic techniques and these will be investigated.

In this project, recrystallisations were tried by slow evaporation of the solutions, diffusion of ether into solutions made up in a variety of solvents and by layering techniques. Water and methanol diffusion systems and slow evaporation of solutions to which bulky non-coordinating anions like PF_6 and BF_4 have been added are to be tried.

Exclusion of the chloride ion from the reaction mixture should lead to new products and tthis should be investigated further. Two possible approaches to achieving this are to either synthesise the dahp as a different salt or to replace the chloride in dahpCl_2 with a different anion after the diamine has ben synthesised.

The second aim of this project was to make an analogue of the H_4**LV5** ligand in which the methyl group was replaced with a charged substituent. To this end synthesis of 2,6-diformyl-4-sulfonyl phenol was undertaken. This compound has been synthesised and isolated. The isolation has proved to be a challenge because of the water soluble nature of this moiety and experimentation with this is continuing. Initial syntheses using this with dahp and $Cu(ClO_4)_2$ are promising. An alternate head-unit could be a carboxylate substituted phenol and a synthesis for this has been found. The carboxylate ester could be used (to overcome the solubility problem) and the ester cleaved after the templating procedure had taken place.

The third section of this research was to develop a ligand capable of binding six metal centres in a planar array. Although complexes containing more than

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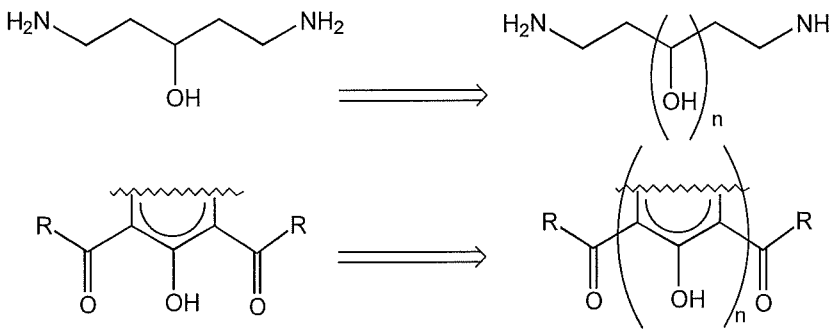
* Except in for cobalt chloride

ester could be used (to overcome the solubility problem) and the ester cleaved after the templating procedure had taken place.

The third section of this research was to develop a ligand capable of binding six metal centres in a planar array. Although complexes containing more than four metal centres are known few of these are planar. There were two reasons for wanting to develop complexes containing multi-metal centres: firstly planar complexes would be better models for metal surfaces and secondly because of an interest in complexes which straddle the boundary between large complexes and the solid state. Two synthetic strategies, as represented in Figure 2, were tried.



H_2daddn was synthesised and reacted with dahp but a closed metal containing macrocycle was not achieved. It is considered that a system in which the acetyl groups are replaced with formyl groups will be needed to accomplish a metal containing macrocycle. Formylation of 1,8-dihydroxy-naphthalene might be possible by the Riemer-Tieman reaction but it seems a more likely route will be one in which the methyl groups are cleaved from H_2daddn.

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